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# JOURNAL

## OF

# THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

**Apparatus for Measuring the Heat of Combustion.** By F. FISCHER (*Ber.*,\* 12, 1694—1696).

**Chemical Constitution of Amalgams of the Alkali-Metals.** By BERTHELOT (*Compt. rend.*, 89, 465).—The solution of the potassium-amalgam  $Hg_4K$ , in four times its weight of mercury, absorbs  $-8.0$  kilogram-degrees of heat, and in twenty times its weight,  $-9.0$  kil-degs. The solution of the sodium-amalgam  $NaHg_{18}$ , in 3 parts of mercury, absorbs  $-2.8$  kil-degs., and in 18 parts,  $-2.9$ . It may thus be concluded that the solution of definite amalgams in different quantities of mercury, like the solution of salts in water, absorbs a constant amount of heat. Only one amalgam of potassium and one of sodium is known in the crystallised form, but from experiments on the varying quantities of heat evolved by the addition of potassium or of sodium to these amalgams, the author concludes that there are two more of each.

The progressive addition of potassium to the amalgam  $Hg_4K$ , evolves nearly constant quantities of heat, until an amalgam,  $8.7Hg + K$ , is obtained; the heat evolved then varies from  $8.7$  to  $5.7$ , and remains constant from  $5.7$  to  $2.9$ . There exist, therefore, two more amalgams of potassium, the first having the composition  $Hg_8K$ , and evolving in its formation  $+29.3$  kil-degs. ( $Hg$  liquid), or  $+27.1$  ( $Hg$  solid), the last figure being identical with that for  $Hg_4K$ . The formula of the other amalgam, that richest in potassium, cannot be calculated with any degree of accuracy. The progressive addition of sodium to the amalgam  $Hg_{18}Na$ , evolves constant quantities of heat up to  $8.1 Na$ , and is also constant from  $8.1$  to  $3.5 Na$ . It is probable,

\* The "Berichte der deutschen chemischen Gesellschaft" will in future be abbreviated to "Ber."

therefore, that two sodium-amalgams,  $Hg_2Na$ , and  $Hg_7Na_2$ , may exist.  
C. W. W.

**Condition of Alkaline Phosphates in Aqueous Solution.** By J. M. VAN BREMMELEN (*Ber.*, 12, 1675—1678).—When a solution of trisodic phosphate is subjected to dialysis, the soda diffuses rapidly, and a small quantity of disodio-hydric phosphate is formed in the dialyser. This experiment shows that trisodic phosphate undergoes partial dissociation when dissolved in water. Disodio-hydric phosphate, dihydro-sodic phosphate, and microcosmic salt do not dissociate under these circumstances.  
W. C. W.

## Inorganic Chemistry.

**Purification of Hydrogen.** By A. LIONET (*Compt. rend.*, 89, 440).—Metallic copper removes all the impurities from hydrogen, except hydrogen phosphide, hydrogen silicide, and hydrocarbons. Cuprous oxide removes all but hydrogen silicide and the hydrocarbons. Cupric oxide removes all but the hydrocarbons. The best form of cupric oxide is that precipitated by potash from a solution of cupric sulphate, and dried at  $100^\circ$ .  
C. W. W.

**Non-existence of Nascent Hydrogen.** By D. TOMMASI (*Chem. News*, 40, 171).—*Reduction of Potassium Perchlorate.*—It was found that when chemically pure potassium perchlorate was submitted to the action of various reducing agents, giving nascent hydrogen, it did not undergo reduction, although it is easily transformed into chloride by the action of a compound which does not set hydrogen free, viz., sodium-hydrogen sulphite. The author asks, how can it be explained that this same perchlorate which undergoes no reduction by means of nascent hydrogen, as shown by sixteen different reactions, can be reduced by the hydrogen disengaged by the action of zinc on sodium-hydrogen sulphite. Although Wurtz declares himself to be in favour of the nascent state of bodies, it appears to the author unlikely that when hydrogen is set free by a reaction, it can be in the state of isolated atoms. It is known that copper, even when finely divided, is but very slightly attacked by hydrochloric acid at the ordinary temperature, although copper hydride is decomposed very energetically. "How can this fact be explained," justly remarks Wurtz, in his Atomic Theory, "if to the affinity of chlorine for copper be not added the affinity of the two atoms of hydrogen to form a molecule?" This reasoning may be said to apply equally to all the reactions producing hydrogen; for example, we know that by the action of hydrochloric acid on zinc, there neither is nor can be any hydrogen in the state of isolated atoms, as Wurtz thinks, and the special properties of nascent hydrogen can be attributed only to the heat which accompanies hydrogen while it is being set free. It is therefore impossible to conclude that hydrogen can be active only in the molecular state, as hun-

dreds of examples prove to us that in many cases it is not the molecule of hydrogen that acts, but its atom.

In conclusion it is mentioned that the recent results of Gladstone and Tribe coincide entirely with the above hypothesis. These chemists, as is known, consider the different allotropic states of hydrogen as ordinary hydrogen in different physical conditions. D. B.

**Active Condition of Oxygen induced by Nascent Hydrogen.** By F. HOPPE-SETLER (*Ber.*, 12, 1551—1555).—Every attempt to explain the vital processes of animals and plants necessarily implies the assumption of a cause whereby the oxygen is rendered active. Hydrogen is evolved in the free state only when oxygen is not present; and most curiously, in presence of oxygen, nascent hydrogen leads to energetic oxidation of any oxidisable substance which may happen to be present. This is specially the case with ferments. The author has proved the fact by two very striking examples. The alloy of palladium with hydrogen discovered by Graham, when placed in oxygen, gives rise to water, owing to combination of the hydrogen of the alloy with the oxygen. This, of course, is well known, but it is not so well known that if indigo be present it is decolorised, and then destroyed; that a mixture of starch with potassium iodide is first turned blue, and that the starch is then completely oxidised; that ammonia is oxidised to ammonium nitrite; that benzene is oxidised to phenol; and that toluene yields benzoic acid. Perhaps a still more remarkable instance is the oxidation of rock-oil by metallic sodium in presence of the small quantity of aqueous vapour which comes in contact with it. The products appear to be acetic and caproic acid, and perhaps butyric acid; and the hard crust which forms round sodium, when it is kept under rock-oil, is really a product of oxidation of the oil, and in fact may be made to yield a number of the higher members of the fatty acid series. It thus appears to be the case that when nascent hydrogen acts on oxygen, it renders the latter gas also nascent, or at least active.

W. R.

**Is Ozone produced during the Atmospheric Oxidation of Phosphorus?** By C. T. KINGZETT (*Chem. News*, 40, 96).—It is generally believed that ozone is produced during the atmospheric oxidation of phosphorus, but the author considers it to be improbable that ozone is formed by the aerial oxidation of phosphorus, considering the constitution of ozone. Moreover, as peroxide of hydrogen is the only known agent which resembles ozone in its general properties, and it is known that hydrogen peroxide is produced in various processes of slow oxidation, it would seem likely that it is this substance which is produced in connection with the oxidation of phosphorus. In addition to various objections which the author has pointed out to viewing the active agent produced in the atmospheric oxidation of turpentine as ozone, there are many considerations which lead to the conclusion that the active agent is peroxide of hydrogen.

There is no known process of slow oxidation which has been established to produce ozone. In various writings on this subject observers have always relied on properties which are common to ozone and hydrogen peroxide, and have never instituted volumetric inves-

tigations, which are alone sufficient to decide the question. On the other hand, several processes of slow oxidation are known, in which peroxide of hydrogen is formed, as for instance, those relating to ether and the terpenes; and it is thought that as hydrogen peroxide is formed in each of these cases as a secondary product, due to the action of water on a peroxide, so also the oxidation of phosphorus by air gives rise to an oxide which generates peroxide of hydrogen by contact with water.

In conclusion, the author mentions that until it has been proved that the active agent produced in the aerial oxidation of phosphorus has the volumetric relations of ozone, such very decided statements as are to be found in chemical text-books should not be made. D. B.

**New Method of forming Hyponitrites and Hydroxylamine.** By W. ZORN (*Ber.*, 12, 1509—1511).—This consists in the electrolysis of a nitrite, using mercury electrodes. Thorpe describes an experiment in which he passed a current from platinum electrodes through a solution of potassium nitrite, and at the negative pole only hydrogen was evolved. On using mercury electrodes, however, if the current is stopped as soon as ammonia begins to be evolved, the liquid, after neutralisation and addition of silver nitrate, gives a copious precipitate of silver hyponitrite. In this reduction, hydroxylamine is also formed, and it is necessary to remove it from the solution by precipitation with mercuric oxide, before adding silver nitrate to precipitate the hyponitrous acid. Four Bunsen's elements are sufficient for this reaction; it is recommended as an advantageous method of preparing hyponitrites. W. R.

**Experiments tending to show the Non-elementary Character of Phosphorus.** By N. LOCKYER (*Compt. rend.*, 89, 514).—Phosphorus heated in a tube with copper gives a gas exhibiting the spectrum of hydrogen; heated alone, phosphorus gives no gas. Phosphorus at the negative pole of a battery in a tube-apparatus (of which a drawing is given), gives a large quantity of gas which shows the spectrum of hydrogen, and is not phosphoretted hydrogen.

C. W. W.

**Compounds of Hydracids with Ammonia.** By E. J. MAUMÉNE (*Compt. rend.*, 89, 506).—In the preparation of ammonium sulphide, the hydrogen sulphide which passes through the first bottle carries ammonia with it, and colourless crystals are deposited in the connecting tube. These crystals have the composition  $\text{NH}_3 \cdot \text{HS}$ . When they are added to strong aqueous ammonia at  $0^\circ$ , colourless crystals are deposited in a few hours having the composition  $(\text{NH}_3)_8 \cdot \text{HS}$ .

The author imagines the existence of two series of ammonium-compounds containing respectively excess of ammonia and excess of hydrogen sulphide, 1 mol. of one of the constituents being united with  $(2, - 1)$  molecules of the other. Members of one series may unite with members of the other series, producing compounds like  $\text{HS}(\text{NH}_3)_{15} \cdot 2[(\text{HS})_7 \cdot \text{NH}_3] = (\text{HS})_{15}(\text{NH}_3)_{17}$ , which might be mistaken for  $(\text{NH}_3)_8 \cdot \text{HS}$ .

The compounds of ammonia with hydrochloric acid present analogies with the above compounds.

C. W. W.

**Oxygen-acids of Sulphur.** By E. J. MAUMÉ (Compt. rend., 89, 422).—The action of iodine on barium thiosulphate gives rise to tetrathionic acid, as observed by Fordos and Gelis, but seven other acids should be produced, according to the proportions of iodine and thiosulphate employed. The acids,  $\text{H}_2\text{S}_2\text{O}_4$  and  $\text{H}_2\text{S}_3\text{O}_6$ , have been obtained. The latter is prepared by mixing 3 mols. of barium thiosulphate and 2 atoms of iodine. The mixture becomes colourless in three or four days. It is then filtered through cotton-wool, and the crystals remaining behind are washed with alcohol. They are then pure and have the composition  $\text{BaS}_3\text{O}_6$ ; with silver nitrate, this salt gives a white precipitate, turning black, and the liquid at the same time becomes acid. The sodium salt crystallises in large, colourless, very soluble crystals, containing a large quantity of water.

G. W. W.

**Basicity of Dithionic Acid.** By H. KOLBE (*J. pr. Chem.* [2], 19, 495—487).—As the author has been unable to obtain an acid salt of this acid or a neutral salt containing two bases, he doubts the correctness of the usually accepted view of the bibasicity of this acid, and is now inclined to the original supposition of Berzelius that it is a monobasic acid, and is represented by the formula  $\text{SO}_3\text{OH}$ . In fact, that it contains the radicle  $\text{SO}_2$ , but united with only one atom of hydroxyl, that is, joined with only one atom of hydrogen by one atom of oxygen. On this supposition sulphur must exist in this acid as a pentad.

That the radicle sulphoxyl ( $\text{SO}_2$ ) may exist as a dyad in sulphuric acid, and as a monad in dithionic acid, appears to the author to be not more improbable than the tetrad and dyad atomicities of tin in stannic and stannous compounds.

A. J. C.

**Behaviour of Calcium Oxide with Carbonic Anhydride.** By K. BIMBAUM and M. MAHU (*Ber.*, 12, 1547—1561).—The object of the experiments described in this paper was to ascertain at what temperature calcium oxide begins to absorb carbonic anhydride, and at what temperature calcium carbonate begins to dissociate. It was found that the lowest temperature at which absorption takes place is the melting point of zinc,  $415.3^\circ$ , and that the carbonate dissociates partially at that temperature, although dissociation begins at a much lower one. The amount of anhydride absorbed by the oxide is about half an equivalent.

W. R.

**Calcium Phosphite.** By R. ROTHE (Pharm. J. Trans. [3], 10, 286).—By adding sugar to a solution of calcium hypophosphite, the latter is precipitated, a circumstance which is generally unknown, and hence it is highly probable that a dense syrup of the mixed hypophosphites contains little if any calcium salt. In the presence of iron, a precipitate is also formed; the proportion of sugar, however, has no share in this change. Ferric hypophosphite, when contained in such a sugar, is said to revert easily to the ferrous form, and it was found that the ferrous salt readily oxidises even in the presence of sugar, forming the dark green and very soluble ferroso-ferric hypophosphite. Ferric hypophosphite occurs in several modifications, of which the crys-



talline variety is almost insoluble in hypophosphorous acid, and hence it is this compound which deposits from the syrup. It was attempted to regenerate this sediment by reducing it to the ferrous condition by the intervention of sulphurous acid. However, the latter was decomposed into sulphuric acid, sulphur, and oxygen, which reacted with the hypophosphorous acid of the sediment, and converted it into phosphorous acid. When solutions of calcium hypophosphite and sodium sulphite are mixed, calcium sulphite is precipitated, which is redissolved by hydrochloric acid, no further reaction setting in until both the hypophosphorous and sulphurous acids are entirely freed by the addition of enough hydrochloric acid. The solution, after filtering off the sulphur, yields, on the addition of ammonia, a crystalline precipitate of calcium phosphite. The latter, however, contains less than half of the phosphorous acid generated, owing to the fact that hypophosphorous acid is monobasic, whilst phosphorous acid is dibasic, and also that a small loss of calcium is incurred as sulphate. By treating the liquid filtered from the sulphur with calcium carbonate, a much larger amount of phosphite is thrown down than with ammonia. The addition of a solution of calcium chloride to the filtrate causes a further precipitation of phosphite, which becomes more distinctly crystalline, and subsides more rapidly when a very little ammonia has been added to the precipitate.

Calcium phosphite is a white crystalline powder, which when heated in a test-tube evolves spontaneously inflammable hydrogen phosphide accompanied by slight detonations. At a certain temperature, it suddenly becomes incandescent, and leaves a residue of calcium phosphate. D. B.

**Zirconium Derivatives.** By S. R. PAYKÜLL (*Ber.*, 12, 1719).—The moist hydrated oxide,  $\text{ZrO}(\text{OH})_2$ , absorbs carbonic anhydride from the atmosphere. By treating zirconium sulphate with the hydrate, one amorphous and two crystalline basic salts were obtained, viz.,  $\text{ZrO}_2 \cdot \text{SO}_3 + x\text{H}_2\text{O}$ ,  $3\text{ZrO}_2 \cdot 4\text{SO}_3 + 15\text{H}_2\text{O}$ , and  $6\text{ZrO}_2 \cdot 7\text{SO}_3 + 19\text{H}_2\text{O}$ . The sulphate forms with potassium sulphate basic double salts, e.g.,  $\text{K}_2\text{O} \cdot \text{SO}_3 + 2(\text{ZrO} \cdot \text{O}_2 \cdot \text{SO}_3) + 14\text{H}_2\text{O}$ . W. C. W.

**Researches on Erbium.** By LECOQ DE BOISBAUDRAN (*Compt. rend.*, 89, 516).—The author examined the spectrum of erbium from various sources, and with one exception the spectra thus obtained exhibited identical lines of the same intensity. The exception was the erbium derived from samarskite. The principal differences were that with samarskite-erbium, the ray in the green,  $\lambda = 536.3$ , is much more intense than the ray  $\lambda = 540.9$ , whilst in the other erbiums the difference is but slight; and the line in the red,  $\lambda = 640.4$ , is as strong, or stronger, than  $\lambda = 653.4$ : whereas in the other erbiums, the line  $\lambda = 653.4$  is much stronger than  $\lambda = 640.4$ .

Two specimens of erbium were taken, one nearly pure, giving the normal spectrum, the other from samarskite, and containing a large quantity of yttria. On fractionation by means of ammonia and subsequently by potassium or sodium sulphate, a portion was obtained from the first which gave a spectrum resembling that of the second,

and a portion was obtained from the second giving a spectrum like that of the first.

The author is continuing this research.

C. W. W.

**Two New Elements in Erbium.** By P. T. CLEVÉ (*Compt. rend.*, 89, 478).—In attempting to obtain pure erbium, the author was led to suspect the existence of two other earths in the erbium obtained. The mixture was therefore fractionated, and the different fractions examined spectroscopically. It was found that, in addition to bands common to all, one band  $\lambda = 6840$  was strong in the residues rich in ytterbium, and wanting in those containing yttrium and erbium, whilst two others,  $\lambda = 6400$  and  $5360$ , were strong in the yttrium and ytterbium residues.

The colour of the fraction treated for ytterbium was a violet-rose, whilst the yttrium fraction had an orange tint.

The metal characterised by the first band,  $\lambda = 6840$ , the author proposes to name *thulium*; it would have an atomic weight of about 113 (the oxide being  $\text{TmO}$ ). Pure erbium, to which must be attributed the common bands, has probably an atomic weight of 110—111. Its oxide has a clear rose colour. The third metal, *holmium*, is characterised by the bands  $\lambda = 6400$  and  $5360$ : it should have an atomic weight less than 108; its oxide seems to be yellow.

C. W. W.

**Spectra of the Earths of the Yttrium-group.** By J. L. SORET (*Compt. rend.*, 89, 521).—The author considers that the new earth, *holmia*, discovered by Clève, is identical with an earth discovered by Delafontaine and Marignac, whose absorption-spectrum was described by himself (*Compt. rend.*, April 29, 1878), and to which Delafontaine gave the name *philippia*. Clève's holmium is characterised by two bands  $\lambda = 640$  and  $\lambda = 536$ , and these two belong likewise to philippium, which is characterised by several other bands.

Clève's second earth, *thulia*, is characterised by a red ray  $\lambda = 684$ . The author claims to have indicated the existence of this element also (*Arch. Sci.*, 63, 99). Marignac also showed the probable existence of this earth in the products rich in philippia and having a low equivalent.

C. W. W.

**Scandium.** By P. T. CLEVÉ (*Compt. rend.*, 89, 419).—This metal occurs only in gadolinite (0.002 to 0.003 per cent.) and yttritanite (0.005 per cent.). Scandium forms but one oxide, scandia,  $\text{Sc}_2\text{O}_3$ ; the composition of which is proved by that of potassium scandium oxalate, and of the double sulphates of scandium with the sulphates of potassium and with ammonium. 8 to 10 grams of scandium oxide, having a molecular weight of 106, agreeing with the number obtained by Nilson, yielded, by repeated decompositions of its nitrate, about 1 gram of a white oxide. This was converted into sulphate, and 1.451 grams of this sulphate yielded 0.5293 gram of scandium oxide.

The atomic weight of the metal is therefore 44.91, and the molecular weight of the oxide, considered as  $\text{ScO}$ , is 45.94 ( $? 60.91 = 44.91 + 16$ ), differing greatly from the lowest number found by Nilson, viz., 105.83. The author considers that this is due to a large

admixture of ytterbia in Nilson's scandia. The atomic weight, as determined by the decomposition of the nitrate, is 45.12. The atomic weight of scandium may therefore be taken as 45.

*Scandium oxide* or *Scandia*,  $\text{Sc}_2\text{O}_3$ , is a light, white, infusible powder of sp. gr. 3.8, resembling magnesia; it is scarcely soluble even in strong acids, but more so than alumina. Sulphuric acid converts it into a bulky white mass of sulphate; hydrochloric acid dissolves the oxide more easily than nitric acid.

*Scandium hydrate* is a bulky white precipitate, drying up to semi-transparent fragments. It does not absorb carbonic acid from the air, is insoluble in ammonia or in potash, and does not decompose ammonium salts when heated with them.

Scandium salts are colourless or white, and have an acid, astringent taste, very different from the sweet taste of the salts of the yttrium metals. The sulphate does not form distinct crystals; the nitrate, oxalate, acetate, and formate, are crystallisable. The chloride exhibits the following reactions:—It gives no spectrum when heated in a gas flame. Potash and ammonia produce bulky white precipitates, insoluble in excess; tartaric acid prevents the precipitation by ammonia in the cold, but on heating an abundant precipitate falls. Sodium carbonate gives a precipitate, soluble in excess. Sulphuretted hydrogen produces no change; ammonium sulphide precipitates the hydrate. Sodium orthophosphate gives a gelatinous precipitate. Oxalic acid gives a curdy precipitate, quickly becoming crystalline; this precipitate dissolves in strong acids, and cannot be completely reprecipitated. Although it appears more soluble than the oxalates of the other yttrium metals, it is found in the first precipitates in the fractional precipitation of a mixture of scandium and ytterbium by oxalic acid. Acid potassium oxalate precipitates a crystalline double salt. Sodium hyposulphite precipitates a boiling solution easily, but incompletely. Sodium acetate behaves similarly. The sulphates of potassium and sodium precipitate crystalline double salts, soluble in a saturated solution of the precipitant.

The author describes in a previous paper (*Bull. Soc. Chim.*, 31, 486) the chloride, nitrate, and sulphate of scandium; the double sulphates,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 2\text{K}_2\text{SO}_4$ ,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{Sc}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ ; the double oxalate,  $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ; the acetate, the formate, and selenite,  $3\text{Sc}_2\text{O}_3 \cdot 10\text{SeO}_3 \cdot 4\text{H}_2\text{O}$ .

The existence of scandium was predicted by Mendelejeff, and its properties described under the name of *ekabor* (*Annalen, Sup.*, 8, 133). The following table shows a comparison of the observed properties of scandium with those predicted of *ekabor*.

*Supposed Characters of Ekabor.*

Atomic Weight = 44.

*Ekabor* should have but one stable oxide,  $\text{Eb}_2\text{O}_3$ , a stronger base than alumina, which it should resemble in many respects. It should be less basic than magnesia.

*Observed Characters of Scandium.*

Atomic Weight = 45.

Scandium forms only one oxide,  $\text{Sc}_2\text{O}_3$ , more energetic than alumina, and less so than magnesia.

Ekabor oxide should resemble yttria, although less basic. The separation of these two earths will be difficult, depending on differences of solubility or of basicity.

Oxide of ekabor is insoluble in alkalis; it will probably not decompose ammonium salts.

The salts should be colourless, and give gelatinous precipitates with  $\text{KHO}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{HNaSO}_2$ .

The sulphate should form a double salt with  $\text{K}_2\text{SO}_4$ , having the composition of alum, but not isomorphous with it.

But few ekabor salts should crystallise well.

The anhydrous chloride should be decomposed by water, giving off hydrochloric acid.

The oxide is infusible and soluble with difficulty in acids after ignition.

The density of the oxide would be about 3.5.

Scandia is less basic than yttria, and their separation depends on differences of solubility between their nitrates.

Scandium hydrate is insoluble in alkalis; it does not decompose ammonium chloride.

The salts are colourless, and give gelatinous precipitates with  $\text{KHO}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{HNaSO}_2$ .

Potassium-scandium sulphate is anhydrous, but otherwise corresponds in composition with alum.

Scandium sulphate does not form distinct crystals, but the nitrate, acetate, and formate crystallise well.

The crystallised chloride is decomposed by heat, giving off hydrochloric acid.

The oxide is an infusible powder, nearly insoluble in acids after ignition.

The density of the oxide = 3.8.  
C. W. W.

**Absorption of Nitrogen Dioxide by Ferrous Salts.** By J. GAY (*Compt. rend.*, 89, 410).—Peligot assigned the formula  $4\text{FeSO}_4 \cdot \text{N}_2\text{O}_2$  to the compound of nitrogen dioxide with ferrous sulphate. The author finds that the composition of this body depends on the temperature and on the pressure of the residual nitrogen dioxide.

At temperatures up to  $8^\circ$  and at the ordinary pressure, the compound formed has the formula  $3\text{FeSO}_4 \cdot \text{N}_2\text{O}_2$ ; from  $8^\circ$  to  $25^\circ$ , at the atmospheric pressure, it has the formula  $4\text{FeSO}_4 \cdot \text{N}_2\text{O}_2$ ; at temperatures above  $25^\circ$  nitrogen dioxide is rapidly given off, and the compound  $5\text{FeSO}_4 \cdot \text{N}_2\text{O}_2$  is produced.

All these compounds exhibit very marked tensions of dissociation, a fact which explains their decomposition in a vacuum; they are also decomposed by a current of hydrogen.

Reducing agents, such as ferrous oxide, reduce the nitrogen dioxide, a mixture of monoxide and free nitrogen being evolved, while the temperature rises sensibly.  
C. W. W.

**Nitrosothioferrates.** By J. O. ROSENBERG (*Ber.* 12, 1715—1717).—By the action of potassium nitrite and ammonium sulphide on a ferrous salt, Roussin (*Ann. Chim. Phys.* [3], 52, 285) obtained a black substance, which was afterwards examined by Porcizinsky (*Annalen*, 125, 302), Demel (*Ber.*, 12, 461), and Pawel (*ibid.*, 12, 1407). This is named by the author *ammonium nitrosoferrothioferrate*.

On the addition of an alkali ferrous oxide is precipitated, and potassium nitro-othioferrate is obtained. The free acid which is liberated when this salt is treated with hydrochloric acid, combines with alkaline sulphides to form a red salt, to which the name *nitroso-ferrous potassium sulphide* is given.

Salts corresponding with each of the two first-mentioned acids have been prepared. They are all converted into nitroprussides by the action of potassium cyanide.

W. C. W.

**Potassium and Ammonium Ferric Chromates.** By C. HENSEN (*Ber.*, 12, 1656—1658).—These salts separate out in dark-red plates containing 4 mols.  $H_2O$  [ $K$  or  $NH_4$ ], when a solution containing ferric chloride and ammonium or potassium dichromate, is slowly evaporated. They have the formula  $K_2CrO_4.Fe_2(CrO_4)_3.4H_2O$ . The ammonium salt is decomposed by cold water and also by the action of heat.

W. C. W.

**Contributions to the Chemistry of the Chromammonium-compounds.** By S. M. JØRGENSEN (*J. pr. Chem.* [2], 20, 105—145).—I. *Chloropurpureo-chromium Salts*.—The starting point for these salts is the chloride,  $Cl_3(Cr_2.10NH_3)Cl_4$ . This is prepared by reducing violet chromic chloride in a stream of pure dry hydrogen, at a red heat, and adding it to a solution of ammonium chloride in strong ammonia (25 grams  $Cr_2Cl_6$  reduced to  $Cr_2Cl_4$ , 90 grams  $NH_4Cl$ , 0.5 litre ammonia). Air is then passed through the blue liquid until oxidation is complete. Two litres of crude hydrochloric acid are added, and the mixture is boiled for some minutes, during which chloropurpureo-chromium chloride separates as a carmine-coloured powder. The crude chloride is washed with a mixture of equal volumes of hydrochloric acid and water, dissolved in very weak sulphuric acid, and filtered into a great excess of strong cold hydrochloric acid. The resulting precipitate is boiled with hydrochloric acid, and washed first with a mixture of acid and water, then with alcohol, and finally dried in the air at the ordinary temperature. This chloride is also a bye-product in preparing Clève's tetramine chloride by the following process:—Ammonium dichromate is reduced by boiling with hydrochloric acid and alcohol, and after addition of ammonium chloride the liquid is evaporated to dryness. The dry residue is then dissolved in strong ammonia; strong hydrochloric acid is added, and the crystals which are deposited on standing are washed first with a mixture of equal parts of hydrochloric acid and water until free from ammonium chloride, then with water, and finally dried. It consists of a mixture of chromium-tetramine chloride and chloropurpureo chloride. This mixture must be protected from the action of light during the remaining operations. It is dissolved in cold water, and shaken with a solution of one part of ammonium sulphate in five parts of water. The tetramine chlorosulphate precipitates in crystals; the filtrate containing the purpureochloride is mixed with hydrosilicofluoric acid, and gives a precipitate of chloropurpureo-chromium silicofluoride. After being washed, it is treated with dilute hydrochloric

acid, to reconvert it into chloride; after reprecipitation with strong acid and washing, first with dilute acid and then with alcohol, it is quite pure. The two salts may also be separated by taking advantage of the insolubility of the compound  $\text{Cl}_2(\text{Cr}_210\text{NH}_3)(\text{Hg}_2\text{Cl}_2)_2$ , produced by adding mercuric chloride to the mixture. The mercury-compound after washing is easily reconverted into the chloride by treatment with hydrochloric acid.

Chloropurpureo-chromium chloride is a red crystalline powder, of a purer red colour than the corresponding cobalt-compound. It appears to crystallise in octohedra of sp. gr. 1.687. It dissolves in 154 parts of water at  $16^\circ$ , and forms a violet-red solution, which, on exposure to light, deposits chromium hydrate. When it is kept, even in the dark, or boiled, roseochromium chloride is produced. It gives the following reactions:—With sodium hypochlorite, nitrogen is evolved, and the chromium is oxidised to chromic acid. Its solution gives a precipitate with strong hydrochloric acid, owing to the insolubility of the chloride in acid. With hydrobromic acid, it gives a crystalline precipitate of the bromide, and with solid potassium iodide one of the iodide. When boiled with potassium cyanide, it turns yellow. Strong nitric acid precipitates the chloro-nitrate. Hydrosilicofluoric acid throws down the red crystalline chlorosilicofluoride. Platinic chloride precipitates, even from a very dilute solution, the chloropurpureo-chromium platinochloride. Sodium platino-bromide gives an analogous precipitate. Mercuric chloride gives red needles of the double salt. Precipitates are also produced by potassium mercuribromide and iodide, by sodium dithionate, potassium chromate, and dichromate, ammonium molybdate, and phosphomolybdate, and by picric and oxalic acids. In these respects this salt closely resembles the analogous cobalt salt. On treatment with silver nitrate only four atoms of chlorine are removed, and the chloro-nitrate is formed. By rubbing the solid chloride with silver oxide and water, roseochromium hydrate is formed. It is a deep red alkaline liquid, which gives a yellowish-red precipitate of roseochromium bromide with strong hydrobromic acid; this, when boiled with hydrobromic acid, changes to bromopurpureo-chromium bromide. In the chloro-chloride, the radicle chlorine is so firmly combined that hot strong sulphuric acid does not expel it; the product is acid chloro-sulphate.

Towards reducing agents, however, the chromium series differ in behaviour from the cobalt series, for the chromium is not so easily reduced. With sulphuretted hydrogen, or with ammonium sulphide, the purpureo-cobalt-compounds give cobalt sulphide, but the purpureo-chromium compounds suffer no change, except the formation of a crystalline purpureopolysulphide, if the ammonium sulphide contains much free sulphur. The cobalt salts are also reduced by potassium ferrocyanide, whereas the chromium salts give a precipitate of ferrocyanide of chloropurpureo-chromium.

The latter part of this paper is occupied with detailed descriptions and analyses of numerous salts of chloropurpureo-chromium chloride, prepared by double decomposition. They have all a red or orange-red colour, and closely resemble the corresponding salts of chloropurpureo-cobalt.

W. R.

**Behaviour of Copper-Ammonium Chloride with Ferrous Sulphide.** By W. F. K. STOCK (*Chem. News*, 40, 159).—In the course of recent experiments on the accurate determination of carbon in iron and steel containing much sulphur, it appeared desirable to ascertain definitely in what manner the reagent used for the carbon separation acted on the iron sulphur compound, but as the composition of that compound is unknown, it was thought best to experiment with a sulphide of known quality. The process used for the carbon separation was McCreath's method based on treating a weighed quantity of iron or steel with a hot concentrated solution of copper ammonium chloride.

From the results, it was evident that the actions of the double copper ammonium salt upon iron carbide and upon iron sulphide were precisely analogous, and that the method held out no hope of separation. It only remained to find to what extent the decomposition had proceeded during the exposure, which was for half an hour at nearly boiling heat. It is shown that allowing for oxidation during washing, &c., it may safely be assumed that 80 per cent. of the original sulphide was decomposed by the double copper salt with liberation of the corresponding amount of free sulphur.

A second experiment was made with native ferric sulphide, which was very finely powdered and exposed at boiling heat for over an hour to the copper solution, but although some free sulphur was obtained, the decomposition was far from complete. D. B.

**Action of the Haloïd Acids on the Sulphates of Mercury.** By A. DITTE (*Ann. Chim. Phys.* [5], 17, 120—128).—It has been stated that dry hydrochloric acid gas decomposes mercuric sulphate, forming mercuric chloride and free sulphuric acid, and that since the chloride is more volatile than the acid, the former can be separated by sublimation at a suitable temperature; and further, that hydriodic and hydrocyanic acids act in a similar manner. The author shows that these statements are wholly incorrect.

When dry hydrochloric acid is passed over mercuric sulphate at ordinary temperatures, no reaction ensues: on warming the sulphate, absorption takes place, with disengagement of heat and without formation of water; on heating more strongly, the product sublimes, but the crystals have no resemblance whatever to sublimed mercuric chloride. An analysis of the crystals showed that their composition exactly corresponded with the formula  $\text{HgSO}_4 \cdot 2\text{HCl}$ ; they are very hygrometric, dissolving in water apparently without decomposition. When volatilised they do not disengage hydrochloric acid.

Hydrobromic acid gas acts in a precisely similar manner, forming the compound  $\text{HgSO}_4 \cdot 2\text{HBr}$ .

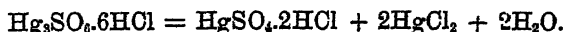
The body  $\text{HgSO}_4 \cdot 2\text{HCl}$  is likewise formed with great facility by gently heating a mixture of sulphuric acid and mercuric chloride, in molecular proportions; or by dissolving the neutral sulphate in hydrochloric acid, and evaporating until crystals are obtained.

The action of hydriodic acid is different; sulphuric acid decomposes mercuric iodide on heating, no compound of the formula  $\text{HgSO}_4 \cdot 2\text{HI}$  being formed. In the same manner, solution of hydriodic

acid in excess, partly or wholly decomposes mercuric sulphate, but no definite combination takes place.

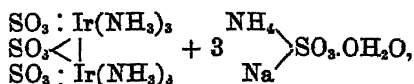
Hydrofluoric and hydrocyanic acids are without action on mercuric sulphate.

Basic mercuric sulphate, *turpeth mineral*, acts with regard to hydrochloric acid in a manner analogous to mercuric sulphate, but it absorbs 6 molecules of HCl for every molecule of sulphate, forming the compound  $\text{HgSO}_4 \cdot 2\text{HgO} \cdot 6\text{HCl}$ ; the latter on being heated strongly, breaks up into the mercuric compound and mercuric chloride, thus:—



A precisely similar compound is formed by the action of either gaseous or liquid hydrobromic acid on *turpeth mineral*. J. W.

**A New Salt of an Iridammonium.** By K. BIRNBAUM (*Ber.*, 12, 1544—1547).—By boiling the double salt of iridic sulphite and sodium sulphite with hydrochloric acid, an acid salt is formed presumably of the formula  $\text{Ir}_2(\text{SO}_3)_3 \cdot 3\text{NaHSO}_3$ . When its solution is saturated with gaseous ammonia, a compound crystallises out in red crusts, having the formula  $\text{Ir}_2\text{Na}_3(\text{SO}_3)_6(\text{NH}_3)_6 \cdot 10\text{H}_2\text{O}$ . The author assigns to it the constitutional formula—



and supposes the  $\text{SO}_3$  group to be in combination with an iridammonium of the formula  $(\text{NH}_3)_6\text{Ir}_2$ . W. R.

## Mineralogical Chemistry.

**Cobalt-glance.** By P. GROTH (*Jahrb. f. Min.*, 1878, 864—865).—In addition to the forms already known to occur on cobalt-glance, the author has observed two dyakisdodecahedrons, two trapezohedrons, and one triakisoctohedron. On cobalt-glance from Tunaberg, Sweden, he observed the following combinations, viz.:—

$$(1.) \frac{\infty\text{O}2}{2} \cdot \text{O} \cdot \infty\text{O}\infty \cdot \frac{3\text{O}\frac{3}{2}}{2} \quad (2.) \frac{\infty\text{O}2}{2} \cdot \text{O} \cdot \frac{1}{2}\text{O}\frac{1}{2} \cdot \frac{1}{2}\text{O}\frac{1}{2}.$$

$$(3.) \frac{\infty\text{O}2}{2} \cdot \text{O} \cdot \frac{2\text{O}\frac{1}{2}}{2} \cdot \frac{\infty\text{O}2}{2} \cdot \text{O} \cdot \frac{2\text{O}\frac{1}{2}}{2}.$$

Crystals from Skutterud, near Modum, in Norway, exhibited the following forms in combination, viz.:  $\frac{\infty\text{O}2}{2} \cdot \text{O} \cdot 2\text{O}$ . C. A. B.

**Cobalt-speis.** By P. GROTH (*Jahrb. f. Min.*, 1878, 865).—Hitherto it has been considered doubtful whether the crystals of this mineral were holohedral or hemihedral, but the author has succeeded in prov-



ing the occurrence of pentagon dodecahedrons, and consequently the isomorphism of cobalt-speis and iron pyrites. On one crystal of cobalt-speis from Wolkenstein  $\frac{\infty O 5}{2}$  and  $\frac{\infty O 10}{2}$  were observed. A large crystal from Schneeberg exhibited the following forms in combination, viz.:  $\infty O \infty . O . \infty O . 2 O 2 . \frac{\infty O 3}{2}$ , and a dyakisdodecahedron, which could not be more nearly determined. C. A. B.

**Sulphide of Silver (Silber-kies).** By A. WEISBACH (*Jahrb. f. Min.*, 1878, 866).—Argyropyrites ( $Ag_3Fe_7S_{11}$ ) occupy an intermediate position, chemically speaking, between sternbergite ( $Ag_3Fe_8S_9$ ) and argentopyrites ( $Ag_3Fe_9S_{15}$ ), and the same fact is observed in regard to its physical properties.

Argyropyrites crystallises in the rhombic system, the crystals from Marienberg being but small, whilst those from Freiberg attained a length of 3 mm. The prisms were terminated either by the basal terminal plane, which was macrodiagonally striated, or else by an obtuse pyramid, the Freiberg crystals being characterised also by a very distinct basal cleavage.

The crystals exhibiting the obtuse pyramids in combination were probably "penetration trillings." C. A. B.

**Bismuth Minerals from Norberg's Mine, Wermland.** By H. SJÖGREN (*Ber.*, 12, 1723).—Bismuth occurs in Wermland: 1st, native, mixed with galena and pyrites; 2nd, as bjelkite,  $2PbS.Bi_2S_3$ ; and 3rd, as the new mineral *galenobismuthite*,  $PbS.Bi_2S_3$ . W. C. W.

**Polysynthetical Twin-crystals of Oriental Spinnelle.** By J. STRÜVER (*Jahrb. f. Min.*, 1878, 865—866).—This paper can only be thoroughly understood by reference to the drawings given. The author concludes that there are three groups of polysynthetical spinelle crystals, viz.: (1.) Those with one twin-axis in common. (2.) Those in which the twin-axes are not parallel to each other, but in which the "twin-face" is common to all, for instance, a form composed of three individuals having a face of  $\infty O$  in common, as twin-plane, and two of their twin-axes parallel to that face. Trillings were also observed resembling a tetrahedron, owing to the predominance of an individual having a tetrahedral development. Sometimes groups composed of four individuals were observed, having all the twin-axes parallel with the twin-planes ( $\infty O$ ). (3.) Those in which there is no parallelism in the twin-axes, nor a twin-plane common to all the forms. C. A. B.

**Manganite.** By P. GROTH (*Jahrb. f. Min.*, 1878, 863—864).—The finest crystals of this mineral are found at Ilfeld, and are characterised by the great number of forms occurring in combination. According to Haidinger, the hemihedry of this mineral is peculiar to the pyramid  $\frac{1}{2} P\bar{2}$ , a fact which appears all the more singular when the great number of pyramids observed on manganite is taken into considera-

tion, and also that, in the case of the isomorphous mineral goethite, no such occurrence is observed. The author, on the contrary, did not observe a single instance of hemihedry, or even twins according to the law "the twin-plane  $\infty P\infty$ ," although he examined one of the finest collections of Ilfeld manganite crystals. The results of his investigation are briefly as follows:—1. Manganite must be considered as a holohedral mineral, hemihedral combinations being very rare. 2. Manganite crystals can be divided into four types, the first two being characterised by an almost entire absence of twins, according to the law "the twin-plane a face of  $P\infty$ " and the occurrence of intermediate forms, whilst the last two types are characterised by the crystals occurring nearly always as twins according to the above-mentioned law, and a more sharply-defined distinction of the types from each other.

The following table will show this more clearly:—

|                    |   |
|--------------------|---|
| A. Long prismatic  | Type I. Prisms, and basal terminal plane predominating.   |
|                    | Type II. Prisms, with macropyramids as terminals.   |
| B. Short prismatic | Type III. Twins, with somewhat numerous forms in combination, the basal terminal plane and obtuse macrodomes predominating. |
|                    | Type IV. Twins, with very numerous forms in combination, macropyramids predominating.                                       |

From the above table it seems probable that an intimate connection exists between the twin formation and the number of forms occurring in combination. The third and fourth types are the rarest.

C. A. B.

**Occurrence of Manganese in Nordmark's Mine, Wermland.** By A. SJÖGREN (*Ber.*, 12, 1723).—In this locality manganese is found as manganosite,  $MnO$ ; pyrochroite,  $MnOH_2O$ ; hausmannite and manganese-spar, together with brucite, heavy spar, hornblende, and garnet.

W. C. W.

**Vanadinite.** By T. NORDSTRÖM (*Ber.*, 12, 1723).—Vandanite has been found in the Udenäs manganese dioxide mine in West Gothland. A mineral has also been discovered at Fahlun, containing 5 per cent. of selenium.

W. C. W.

**Titanates from Småland.** By C. W. BLOMSTRAND (*Ber.*, 12, 1721—1723).—The following minerals were found at Slättåkra, Ålsheða, occurring in coarse granite:—1. *Polycrase*. 2. *Titaniferous iron ore*, remarkable on account of the water it contained; and 3. A new mineral *ålsheðite*, which appears to occupy an intermediate position as regards composition between yttritanite and goethite. In this compound titanium dioxide plays the part of a base.

W. C. W.

**Pseudomorphs of Calcite after Aragonite.** By G. VOM BATN (*Jahrb. f. Min.*, 1878, 863).—The crystals in question came from Schemnitz, and were from 10 to 20 cm. in length and from 4 to 6 cm.

in breadth: they were terminated apparently by a brachydome, the space originally filled by aragonite being taken up by calcite. One specimen, 7 cm. long, 4 cm. broad, and from 2 to 3 cm. thick, consisted of the outer shell of an aragonite crystal, which was built up out of an aggregate of small, well-developed calcite crystals, exhibiting the following forms in combination, viz.:  $R^3$ . —  $\frac{1}{2}R.\infty R$ , the crystals not occupying any regular position with regard to the original aragonite crystal.

C. A. B.

**Crystal-system of Leucite.** By J. HIRSCHWALD (*Jahrb. f. Min.*, 1878, 867).—Hirschwald stated in a former paper that leucite might be considered as a mineral crystallising in the regular system, with a polysymmetrical development in the sense of the quadratic system. From further investigations he arrives at the conclusion that a difference in opinion about the practical relationships of leucite is possible in the two following cases only, viz.:—1. Is the polysynthetical twin-formation a complete dodecahedral one, or does it only represent the faces of the pyramid? 2. Have the imbedded crystals the interfacial angles (winkelwerthern) of 202, or have the apparently regular forms, without exception, the angles of the acuter lateral edge of the eight-sided pyramid? Hirschwald considers that he has found a complete answer to these questions in the results of his investigations, and states that the imbedded leucite crystals have undoubtedly the interfacial angles of 202, whilst the optical properties prove a complete dodecahedral twin-formation.

C. A. B.

**Composition of Eclogite.** By E. R. RIEBS (*Jahrb. f. Min.*, 1878, 877).—Eclogite is a non-felspathic crystalline rock which, in its simplest forms, consists of omphazite and garnet, whilst the varieties of this rock are produced by the occurrence of quartz, hornblende, cyanite, zoisite, or mica. The accessory minerals are zircon, apatite, titanite, epidote, iron-pyrites, magnetic iron-pyrites, and magnetite. Omphazite occurs as an augite in short, thin prisms of a grass-green colour; the rare smaragdite as a green hornblendic mineral. The garnet often contains numerous enclosures of zircon, quartz, &c., and is occasionally decomposed. Zircon occurs enclosed in large amount (in reddish-brown grains or greyish-yellow prisms, exhibiting P with  $\infty P$  and  $\infty P\infty$ , also twins, parallel to a face of  $P\infty$ ) in the garnet and omphazite. The true eclogite is found imbedded in the strata of the crystalline slates, and is often intimately associated with hornblendic plagioclase garnet-rocks, but not with those containing omphazite.

C. A. B.

**Thaumasite.** By G. LINDSTRÖM (*Ber.*, 12, 1723).—This new mineral, having the composition  $CaOSiO_2 + CaCO_3 + CaSO_4 + 14H_2O$ , is found in the Åreskutan mountains in Jutland.

W. C. W.

**Manganese-nodules from the Bed of the Pacific Ocean.** By C. W. GÜMBEL (*Jahrb. f. Min.*, 1878, 869—870).—These nodules were collected at a depth of 2740 fathoms, between Japan and the Sandwich Islands, by the "Challenger" Expedition. They were either round or long in shape, with a dull, dirty-brown coloured surface, and

enclosed fragments of pumice-stone, and more rarely teeth of sharks or fragments of mussels. A microscopical examination showed that organic life had nothing to do with their formation, which was due to a mechanical concretion of inorganic matter; a kind of oolitic formation on a large scale. The pumice-stone was most probably the result of submarine eruptions; it was trachytic in character, and there was evidence to show that it had lain for a considerable space of time in muddy water, which penetrated it eventually, and left behind a deposition of manganese oxide. The author believes that the nodules in question derived some of their constituents from submarine springs, whilst their form can be accounted for by the action of the waves. An analysis gave the following results:—

|                                  |                                 |                    |                      |                                  |                    |
|----------------------------------|---------------------------------|--------------------|----------------------|----------------------------------|--------------------|
| Fe <sub>2</sub> O <sub>3</sub> . | MnO <sub>2</sub> .              | H <sub>2</sub> O.  | SiO <sub>2</sub> .   | Al <sub>2</sub> O <sub>3</sub> . | Na <sub>2</sub> O. |
| 27·460                           | 23 600                          | 17·819             | 16·030               | 10·210                           | 2·358              |
| Cl.                              | CaO.                            | TiO <sub>2</sub> . | SO <sub>3</sub>      | K <sub>2</sub> O.                | MgO.               |
| 0·941                            | 0·920                           | 0·660              | 0·484                | 0·396                            | 0·181              |
| CO <sub>2</sub>                  | P <sub>2</sub> O <sub>5</sub> . | CuO.               | NiOCO <sub>2</sub> . | BaO.                             |                    |
| 0·047                            | 0·023                           | 0 023              | 0 012                | 0 009 =                          | 101·173            |

The minute quantity of carbonic acid is striking, and it would appear from the above analysis that an energetic oxidation takes place at great depths. The occurrence of these manganese-nodules at the bottom of the sea is of great geological interest, as similar manganese-nodules are common in various sedimentary formations.

C. A. B.

**Occurrence of Lithium in Rocks, Sea Water, Mineral Waters, and Saline Deposits.** By L. DIÉULFAIT (*Ann. Chim. Phys.* [5], 16, 377—391).—*Primary Rocks (Granite, Syenite, Gneiss).*—The author has examined one hundred and thirty-nine specimens from different localities in Europe and Africa, and detected lithium in all of them, although in very different proportions.

*Mother Waters of Salt-marshes.*—The author found these to be so rich in lithia, that by simply dipping a platinum wire into the water and holding it in the flame, the lithium spectrum obtained was as intense as that of sodium. Lithium could always be detected in the waters of from 15—25° B., as at that concentration almost all the gypsum is deposited; the crystals of gypsum themselves, however, contained only excessively minute traces of lithium. The sedimentary deposits forming the bottom of the basins invariably contained it. Lithium was found also in all sedimentary deposits left by the spontaneous evaporation of sea water.

*Sea Water.*—Bunsen succeeded in detecting lithium in 40 c.c. of sea water, but the author found that on evaporating 1 c.c. of the water of the Mediterranean to dryness, treating the residue with alcohol, and evaporating the alcoholic solution, the second residue gave a very distinct lithium spectrum. As lithium was shown to be a constituent of all the primitive rocks, it appeared highly probable that it would be found in all sea waters. The author has detected it in the waters of

the Red Sea, the Indian Ocean, the Chinese Sea, the Atlantic Ocean, the Antarctic Ocean, and the Northern Ocean. Neither Forchhammer nor Credner, in his *Traité de Géologie*, mentions lithium as a constituent of sea water.

The author applies the results of his experiments to test his theory, that deposits of gypsum of all ages have a purely sedimentary origin. This theory has been opposed by geologists, especially as applied to gypsums of the tertiary formation.

*Gypsum of the Tertiary Period.*—*Paris.*—Samples of the pure crystals from the quarries of Montmartre and Pantin were found to be quite free from lithium, although in every case the yellow calcareous deposit adhering to the crystals or embedded in their cavities contained it in such quantity, that .0002 gram was amply sufficient to give the characteristic spectrum.

*Aix and Provence.*—In these localities the gypsum occurs in beds, separated by thin layers of marl. In certain spots, large honey-yellow crystals of gypsum occur, imbedded in a yellowish deposit. In all cases the pure gypsum was free from lithium, whilst the yellow marl contained it in considerable quantity. Similar results were obtained on examining the gypsum from Camoins and Dauphin, near Marseilles, from Vaucluse, and from different parts of Italy. The waters from the *Saffioni* were found to contain lithium in considerable quantity.

*Gypsum of the Secondary Formation*—Forty-eight samples from the Alpine district, eleven from Languedoc, seven from the Pyrenees, three from Lorraine, and four from Wurtemberg, all belonging to the triassic formation, were examined, with results similar to those obtained with the gypsums of the tertiary periods. The samples of pure gypsum were free from lithium, or contained only traces; whilst the associated earthy deposits were invariably rich in this element.

These investigations show a complete analogy between the triassic gypsum deposits, those of the tertiary formation, and those from the salt marshes of the modern period: whence the conclusion that the former two classes of deposits were formed under the same conditions as those we now see causing the formation of gypsum in the salt marshes.

*Mineral Waters of the Primary Formation.*—A characteristic group of these waters is found in France in the Pyrenees district. The following were examined, and in every case lithium was found to be a constituent:—Luchon, Caunterets, Baréges, Saint-Sauveur, Labassère, Visòs, Bonnes, Ax, Amelie.

*Saline Waters.*—Those of Allevard, Balaruc, Bourbonne, Capvern, Contrexeville, Digne, Gréoulx, Mièrs, Montbrun, Montmirail, Pougues, Saint Gervais, Saliès, Salins, Uriège, Vittel, Haurmem Meskoutin (Algiers), La Reine (near Oran), Baden (Switzerland), Birmenstooft (Switzerland), Loèche (Switzerland), Wildegg (Switzerland), Pullna, Hombourg, Kissingen, Kreusnach, Nauchheim, and Soultzmatt, were examined, and lithium found in all; in some cases in such quantity that it could be detected in the evaporation residue of a single drop of the water. This fact, taken in conjunction with the previous experiments, strengthens the author's theory that saline waters are mine-

ralised at the expense of saliferous deposits left by the evaporation of ancient seas.

J. M. H. M.

**Note on the Silesian Basalts and their Mineral Constituents.** By P. TRIPKE (*Jahrb. f. Min.*, 1878, 876—877).—Of these basalts from Upper and Lower Silesia, fifteen were plagioclase basalts, two were nepheline basalts, and one from Wickenstein, near Querbach, was nephelinite. The microscopical characteristics of these basalts were briefly as follows, viz.:—A colourless glass-zone (which was itself surrounded by a glassy wreath of felt-like augite-microlites) surrounded the quartz inclosures, this observation agreeing with that of Lehmann on the inclosures of the basalts of the Lower Rhine. Some of the interfused quartz-fragments were converted into tridymite. The orthoclase was not surrounded by glass substance or augite. Lamellar enstatite occurs alternately with lamellar diallagite in the olivine nodules of the Gröditzberg, the lamellæ being parallel to the macropinacoid of the enstatite. The acicular and tabular inclosures in these minerals the author considers to be negative forms of enstatite and diallagite, filled with opal. The phillipsite from Sirgwitz was monosymmetrical, and exhibited a complicated polysynthetical twin-formation. The basalt of Steuberwitz contains simple augite crystals, and those with a polysynthetical twin-formation. The olivine from Thomasdorf was changed into magnesium carbonate, whilst the nephelinite from Wickenstein contains augites having a zonal structure.

C. A. B.

**Basaltic Lavas of the Eifel.** By E. HUSSAK (*Jahrb. f. Min.*, 1878, 871).—The author made a thorough examination of the above-mentioned basalts, and arrived at the following conclusions, viz.:—(1.) There are no felspathic basaltic lavas in the Upper Eifel, but only nepheline or leucite-basaltic lavas, which differ considerably from the non-melted, mound-forming basalts. (2.) The olivine from the Eifel lava is always fresh; it is not present, however, in the lava from Dockweiler. (3.) The lava from the Eifel contains biotite, in contradistinction to the basalt of the Eifel. (4.) Melilite occurs in considerable quantity in some of the lavas, especially in that from Bongsberg, where it can be microscopically detected. (5.) Hauyn is only present in the lava from Scharteberg. (6.) Perowskite occurs as a characteristic of the lava from Scharteberg, but it is also present in lavas of the Laacher See district (the three last-named minerals do not occur in the basalts of the Eifel). (7.) The chemical analyses of the lavas agree very well with the results of the microscopical examinations. (8.) The tufa of the Kolenberg, near Anel, was found to be true palagonite-tufa, containing, however, leucite and magnetite. (9.) The microscopical examination of this tufa fully confirms Rosenbusch's theory of the formation of the palagonite-tufa. (10.) Mitscherlich's analysis of this palagonite-tufa agrees fully with its microscopical analysis. (11.) The so-called basalt-rock from Lützenberg, near Weierhof, in the Eifel, proves to be a true garnetiferous picrite, the first which has been observed on the left bank of the Rhine. (12.) The garnets in this picrite exhibited a zonal structure, were par-

tially double-refracting, and very probably were the variety called melanite. C. A. B.

**The Meteorite of Vavilovka.** By B. PRENDEL (*Jahrb. f. Min.*, 1878, 868).—Numerous meteorites fell on the 7th of June, 1876, near the village of Vavilovka, in Cherson, Russia, accompanied by a sound resembling thunder. A specimen examined by the author exhibited the characteristic black rind, which was 0·6—1 mm. in thickness, also irregular stripes here and there. A polished surface showed the mass of the meteorite to consist of numerous angular whitish specks. The metallic constituents were particles of nickel-iron disseminated throughout the whole mass, and grains of magnetic-pyrites not, however, magnetic. Sp. gr. = 3·51. Chemical composition as follows, viz. :—

|                    |                                  |                                  |              |
|--------------------|----------------------------------|----------------------------------|--------------|
| SiO <sub>2</sub> . | MgO.                             | Al <sub>2</sub> O <sub>3</sub> . | CaO.         |
| 53·81              | 18·54                            | 8·75                             | 2·07         |
| Alkalis.           | Fe <sub>2</sub> O <sub>3</sub> . | Magnetic pyrites.                | Nickel.      |
| 1·14               | 9·41                             | 5·26                             | 0·70 = 99·68 |

The meteorite belongs to the chondrites.

C. A. B.

**The Meteorite of Grosnaja.** By G. TSCHERMAK (*Jahrb. f. Min.*, 1878, 868—869).—Two specimens which fell on the 28th of June, 1861, at the above locality on the Terek, Caucasus, were examined by the author. They were encrusted with a moderately thick fused surface (*schmelz-rinde*), and were black-grey in colour. The ground mass was massive, black, and opaque, and enclosed numerous light-coloured particles consisting of olivine, enstatite, bronzite, and magnetic iron-pyrites. The bronzite, olivine, and a mineral resembling augite were found together forming nodules in the ground mass, whilst specks of the magnetic iron-pyrites were observed in the inclosures and also in the ground mass. The bronzite-nodules exhibited an incrustation or rind, and the magnetic iron-pyrites occurred zonally on the enclosed minerals. An analysis of the meteorite furnished the following results :—

|                    |                                  |       |      |                        |
|--------------------|----------------------------------|-------|------|------------------------|
| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | FeO.  | CaO. | MgO.                   |
| 33·78              | 3·44                             | 28·66 | 3·22 | 23·55                  |
| K <sub>2</sub> O.  | Na <sub>2</sub> O.               | C.    | H.   | Magnetic iron pyrites. |
| 0·30               | 0·63                             | 0·68  | 0·17 | 5·37 = 100·00          |

Sp. gr. = 3·55. The Grosnaja meteorite is a chondrite one, poor in carbon.

C. A. B.

**Chalybeate Springs of Carlsbad.** By A. ALMÉN (*Ber.*, 12, 1724—1725).—These springs are exceptionally rich in ferrous carbonate.

|                                |      |               |                     |
|--------------------------------|------|---------------|---------------------|
|                                |      | Total solids. | FeCO <sub>3</sub> . |
| No. 1 contains in 10,000 parts | .... | 1·348         | 0·593               |
| " 2                            | "    | 1·653         | 0·669               |
|                                |      |               | W. C. W.            |

**Water of the River Vartry.** By J. FLETCHER (*Chem. News*, 40, 171).—This water shows on analysis very little chlorine, 0·001155 per litre or 0·8025 grain per gallon. It is of great softness, the hardness being only 3° on Clark's scale, and yielding a total solid residue varying, as the result of many experiments, from 4 to 6 grains per gallon.

The results of the author's experiments show that the water is of great purity, chemically considered, but strongly impregnated with peat, having a very decided action on lead when flowing through pipes of that material, although without action on it when at rest, but rather leaving an organic deposit.

D. B.

### Organic Chemistry.

**Specific Gravities of Solid Organic Compounds.** By H. SCHRÖDER (*Ber.*, 12, 1611—1618).—The author has determined the specific gravity and molecular volumes of the following compounds:—

|                               | Sp. gr. | Volume.    |
|-------------------------------|---------|------------|
| Malic acid .....              | 1·559   | 85·9       |
| Dimethyloxamide .....         | 1·281   | 90·5       |
| Diethyloxamide .....          | 1·164   | 123·7      |
|                               | 1·173   | 122·8      |
| Salicylic acid .....          | 1·485   | 92·9       |
|                               | 1·482   | 93·1       |
| Metahydroxybenzoic acid ..... | 1·478   | 93·7       |
| Parahydroxybenzoic acid ..... | 1·476   | 93·5       |
|                               | 1·46    | 94·5       |
| Phthalic anhydride .....      | 1·527   | 96·9       |
|                               | 1·530   | 96·7       |
| Benzoic anhydride .....       | 1·247   | 181·3      |
|                               | 1·284   | 183·2      |
|                               | 1·231   | 183·6      |
| Protocatechuic acid .....     | 1·542   | 99·9—100·6 |
|                               | 1·541   |            |
| Gallic acid .....             | 1·703   | 99·8       |
|                               | 1·685   | 100·9      |
| Mandelic acid .....           | 1·355   | 112·2      |
|                               | 1·367   | 111·2      |
| Phenylacetic acid .....       | 1·236   | 110·0      |
|                               | 1·22    | 111·5      |
| Methylparahydroxybenzoic acid | 1·385   | 109·8      |
|                               | 1·376   | 110·5      |
|                               | 1·364   | 111·5      |
| Cinnamic acid .....           | 1·249   | 118·6      |
|                               | 1·246   | 118·8      |
| Cumic acid .....              | 1·169   | 140·3      |
|                               | 1·156   | 141·9      |



|                              | Sp. gr. | Volume. |
|------------------------------|---------|---------|
| Orcinol .....                | { 1.296 | 109.7   |
|                              | { 1.283 | 110.7   |
| Benzamide .....              | { 1.344 | 90.0    |
|                              | { 1.388 | 91.2    |
| Amidobenzoic acid .....      | { 1.515 | 90.5    |
|                              | { 1.506 | 91.2    |
| Orthonitrobenzoic acid ..... | { 1.576 | 106.0   |
|                              | { 1.574 | 106.1   |
| Metanitrobenzoic acid .....  | { 1.496 | 111.6   |
|                              | { 1.492 | 112.0   |
| Acetanilide .....            | { 1.216 | 111.0   |
|                              | { 1.205 | 112.0   |
| Benzanilide .....            | { 1.321 | 149.2   |
|                              | { 1.306 | 150.8   |
| Thiocarbanilide .....        | { 1.33  | 171.5   |
|                              | { 1.311 | 173.9   |
| Aniline hydrochloride .....  | { 1.227 | 105.6   |
|                              | { 1.216 | 106.5   |
|                              | { 1.201 | 107.8   |
| Aniline nitrate .....        | { 1.360 | 114.8   |
|                              | { 1.356 | 115.0   |
| Aniline sulphate .....       | { 1.377 | 206.3   |
| Naphthalene .....            | { 1.145 | 111.9   |
| Nitronaphthalene .....       | { 1.341 | 129.0   |
|                              | { 1.321 | 131.0   |
| $\alpha$ -Naphthol .....     | { 1.224 | 117.8   |
| $\beta$ -Naphthol .....      | { 1.217 | 118.2   |
| Ammonium benzoate .....      | { 1.264 | 110.0   |
|                              | { 1.26  | 110.3   |
| Calcium benzoate .....       | { 1.457 | 230.6   |
|                              | { 1.435 | 234.1   |

The molecular volumes of the majority of the above compounds are multiples of 5.91, which in a former communication (*Ber.*, 12, 566) was shown to be true for some benzene derivatives.

In the case of some isomerides, the "stere" appears to vary a little from 5.91, as shown by the following:—

|                                    | Volume.     | "Stere." |
|------------------------------------|-------------|----------|
| 1. { Quinol .....                  | 82.6—83.1   | 5.91     |
| { Pyrocatechol .....               | 81.6—82.1   | 5.8      |
| 2. { Parahydroxybenzoic acid ..... | 93.5—94.5   | 5.91     |
| { Metahydroxybenzoic acid .....    | 93.7        | 5.9—5.8  |
| { Orthohydroxybenzoic acid .....   | 92.9—93.1   | 5.8      |
| 3. { Orthonitrophenol .....        | 95.8—96.3   | 6.0—6.05 |
| { Paranitrophenol .....            | 94.5—94.7   | 5.91     |
| 4. { Mandelic acid .....           | 111.2—112.2 | 5.91     |
| { Anisic acid .....                | 109.8—110.5 | 5.8      |
| 5. { Isonaphthol .....             | 118.2       |          |
| { $\alpha$ -Naphthol .....         | 117.8       |          |

The members of the following six groups are isosteric: (1.) Malic and tartaric acids. (2.) Benzoic and paraoxybenzoic acids. (3.) Resorcinol and pyrogallol. (4.) Phenylacetic and anisic acids. (5.) Protocatechuic and gallic acids. (6.) Benzamide and benzoic acids.

In former communications, the author has shown that the elements carbon, hydrogen, oxygen, and nitrogen occupy in the solid state the space of one "stere."

The determinations given above offer further support of this statement, thus: oxamide, dimethyloxamide, and diethyloxamide have molecular volumes differing by  $C_2H_4$ , or 6 steres. In naphthalene and isonaphthol we have difference of  $O_2 = 1$  stere, and in benzoic and orthonitrobenzoic acids we have the difference  $N_2O_2 - H_2 = 2$  steres. Some other examples are given.

From this rule, it follows that the benzene nucleus possesses one stere more than the sum of those of the elementary atoms contained in it. Thus: benzoic acid,  $C_6H_5.COOH = 16 \times 5.91$ . Paranitrophenol,  $C_6H_5.NO_2O = 16 \times 5.91$ , phthalic anhydride,  $C_8H_4O_3 = 16 \times 6.05$ . Orthonitrobenzoic acid,  $C_8H_5.NO_2.CO_2 = 18 \times 5.91$ . Phenylacetic acid =  $19 \times 5.8$ . Naphthalene,  $C_{10}H_8 = 19 \times 5.91$ . Isonaphthol,  $C_{10}H_8.C_4H_4O = 20 \times 5.91$ . Cinnamic acid,  $C_9H_8.C_3H_2.COOH = 20 \times 5.91$ .

P. P. B.

**Formation of Hydrocyanic Acid in the Electric Arc.** By J. DEWAR (*Chem. News*, 39, 282).—From the statements made by Plucker, Ångström, and Thalén, that the so-called carbon lines are invariably associated with the formation of acetylene, the author made experiments with a view to extract this substance from the electric arc, which shows this spectrum at the positive pole when the electric current is powerful and occasionally intermittent. The carbons were used in the form of tubes so that air could be drawn through them, and so that any gas might be passed up one tube and drawn down the other and then examined.

A Siemens and a De Méritens magneto-machine were employed.

In the first experiment a current of air was drawn down the negative pole and passed through solutions of potash and potassium iodide and starch. No nitrates were indicated, but the potash solution contained sulphides.

In the second experiment in which hydrogen was led in by the positive pole and withdrawn by the negative, acetylene was found by the ammoniacal sub-chloride of copper-test, whilst water through which the gases were passed gave distinct evidence of hydrocyanic acid. The hydrogen flame burning alone gave no evidence of these substances.

Air drawn through the negative pole gave considerable quantities of hydrocyanic acid, but when drawn through the positive pole a larger proportion was found, whilst the same carbons used with De Méritens' magneto-machine gave no result.

If the carbons are not purified, hydrogen sulphide is always found along with the other compound.

The author concludes that the high temperature of the positive pole is required to produce the hydrocyanic acid, which is in all probability

formed by the free nitrogen reacting on the acetylene thus:  $C_2H_2 + 2N = 2HCN$ , and that the hydrogen to form the acetylene is obtained from the decomposition of aqueous vapour and from the combined hydrogen in the carbons.

W. T.

**Oxidation of Alcohols by Electrolysis.** By A. RENARD (*Ann. Chim. Phys.* [5], 16, 289—337).—I. *Electrolysis of Alcohols in presence of Water Acidulated by Sulphuric Acid. Methyl Alcohol.*—The purest methyl alcohol of commerce, after being carefully freed from traces of acetone and methyl ethers, was acidified with about 5 per cent. of dilute sulphuric acid (1 : 4), placed in a flask holding from 100—200 c.c., and submitted to the action of a current from 4 Bunsen cells of about a litre and a half capacity. Hydrogen was evolved at the negative pole, and at the positive pole a gas was very slowly given off (at the rate of 25—30 c.c. in 24 hours): it contained  $CO_2$ , 23.9;  $CO$ , 50.0;  $O$ , 26.1. At the end of 48 hours the yellowish liquid was distilled. The distillate was found to contain *methyl formate* and *methylal*. Methyl aldehyde was never found as a product of the electrolysis, being no doubt oxidised to formic acid as soon as formed, or reacting with the methyl alcohol to form methylal. The methylal is one of the chief products of the reaction, and may be prepared quite easily by this method. The residue of the distillation of the electrolysed liquid contained hydrogen methyl sulphate. To show that this was produced by the electrolysis, a mixture of the alcohol with dilute sulphuric acid was prepared and divided into two parts, one being allowed to rest, and the other submitted to electrolysis. The latter was found to contain hydrogen methyl sulphate, whilst the former was quite free from it.

*Ethyl Alcohol.*—The electrolysis of ethyl alcohol has already been attempted by various chemists, amongst others by Riche, D'Almeida and Bontan, and Jaillard. The only products hitherto recognised, besides chloracetic acid and compound ammonias resulting from the hydrochloric and nitric acids employed for acidification, are aldehyde and acetic acid.

The author's experiments were conducted in the same manner as those with methyl alcohol. An abundant evolution of hydrogen occurred at the negative pole; but at the positive pole no gas was disengaged, all the oxygen being absorbed by the oxidation of the alcohol. The process was arrested at the end of 48 hours, and the liquid on being distilled yielded (besides alcohol) *ethyl formate*, a little *aldehyde*, and a large proportion of *ethyl acetate*; small quantities of *acetal* were likewise obtained, and a new substance which the author considers to be *ethylidene monethylate*,  $CH_3.CH(O).EtO$ , i.e., acetal, in which  $C_2H_5$  is replaced by  $H$ . This substance when separated, and purified by fractional distillation, boiled at 88—90° C., and on analysis gave numbers corresponding with the formula  $C_4H_{10}O_2$ . The residue from the distillation of the electrolysed mixture contained hydrogen ethyl sulphate, the formation of which was proved, as in the previous case, to be really due to the electrolysis. Under certain conditions, more than 60 per cent. of the sulphuric acid employed for acidification is transformed into the sulphate.

If the electrolysis of methyl or ethyl alcohol be continued for several days, a point is reached at which the liquid appears to contain nothing but formic or acetic acid; on still prolonging the operation, almost pure oxygen is disengaged at the positive pole, in volume almost exactly half that of the hydrogen, and the liquid is found still to contain a little hydrogen methyl or ethyl sulphate, the decomposition of which is very slow.

*Electrolysis of Hydrogen Methyl Sulphate.*—100 c.c. of a solution containing 20 grams of this ethereal salt, prepared by decomposing barium methyl sulphate with sulphuric acid, was submitted to the action of the current from 4 Bunsen cells. Hydrogen was disengaged at the negative pole, and oxygen containing 5 or 6 per cent. of the oxides of carbon at the positive pole, about 23 volumes of oxygen being evolved for every 100 volumes hydrogen. After 48 hours the liquid was distilled, and the distillate was found to contain formic acid and a solid polymeride of methaldehyde, *trioxymethylene*,  $C_3H_2O_3$ , which was obtained as a white, amorphous, insoluble residue by evaporation of the solution over sulphuric acid in a bell-jar. Similar results were obtained by the electrolysis of a more dilute (5 per cent.) solution of hydrogen methyl sulphate, and also of a similar solution containing a little free sulphuric acid. From this, it would seem that methaldehyde is first produced, a part being at once transformed into the polymeric modification, whilst the other is oxidised to formic acid. No trioxymethylene is produced by electrolysis of methyl alcohol, because the methaldehyde as fast as it is formed, reacts on the methyl alcohol to produce methylal.

*Electrolysis of Hydrogen Ethyl Sulphate.*—This compound was submitted to electrolysis in a manner similar to the corresponding methyl compound, and gave acetic acid and a little formic acid. No aldehyde was found in the distillate, but the odour of aldehyde was perceptible during the progress of the electrolysis.

*Electrolysis of Glycerol.*—Glycerol diluted with two-thirds of its volume of water, acidulated with one-tenth of sulphuric acid, was submitted to the action of the current from 5 Bunsen cells. Hydrogen was disengaged at the negative pole, and at the positive pole a gaseous mixture containing  $CO_2$ , 2.9; CO, 32.8; O, 64.3 volumes. After 48 hours the process was arrested, the liquid saturated with calcium carbonate, filtered, and submitted to distillation without boiling at a low pressure in an atmosphere of carbonic anhydride. On spontaneous evaporation over sulphuric acid, the distillate left a white amorphous residue, which gave on analysis numbers agreeing with the formula  $C_3H_2O_3$ , and which proved to be identical with *trioxymethylene*,  $C_3H_2O_3$ . The yield of this substance is very small, 130 c.c. of the distillate giving about half a gram of the dry substance. Submitted to electrolysis, trioxymethylene gives rise to formic acid, and a gaseous mixture containing, in 100 volumes,  $CO_2$ , 5; CO, 15; and O, 80. By treating a solution of trioxymethylene with sulphuretted hydrogen, a white precipitate is obtained, of the formula  $(C_3H_2S_2O)_2H_2O$ . It differs therefore from the body  $C_3H_2S_2$ , which Hoffmann obtained by acting on trioxymethylene with a mixture of hydrochloric and hydrosulphuric acids. The oxysulphide obtained by the author melts at  $80-82^\circ$ , and solidifies

on cooling to a hard, white, opaque mass, like wax. It is soluble in hot water, insoluble in alcohol and ether, and boils at 180—185° C. By treating the trioxymethylene with ammonia, the author obtained the *hecamethylenamine* of Butlerow,  $C_6H_{12}N_4$ , but was unable to obtain from it the hydrochloride  $C_6H_{12}N_4Cl$ , described by that chemist.

The residue from the distillation of the electrolysed glycerol contained calcium formate, acetate, and glycerate. Besides these substances there is formed by electrolysis of glycerol a small quantity of a glucose isomeric with ordinary glucose, and which is probably a polyemide of trioxymethylene. It is found in the alcohol used to precipitate the lime salts from the distillation residue of the electrolysed liquid. This alcoholic solution also contains the lime salt of a new acid, identical with that formed in the electrolysis of mannitol. The pure glucose is obtained in the form of a yellow-brown syrup, which may be dried at 60° in a current of hydrogen. At 80—100° it blackens, loses water, and gives out the odour of caramel. Its alcoholic solution yields a precipitate with barium hydrate, the composition of which agrees with the formula  $(C_6H_{12}O_6)_4(BaO)_3$ . The glucose reduces silver nitrate, with formation of a mirror, and precipitates cuprous oxide from Fehling's solution on heating. It is oxidised to oxalic acid when heated with dilute nitric acid. Slightly heated with soda its solution darkens strongly. It is very soluble in water and alcohol, is not precipitated by lead subacetate, but forms an abundant precipitate with ammoniacal lead acetate. It appears to be incapable of fermentation by beer yeast. When the electrolysis of glycerol is prolonged for several days, the trioxymethylene and glucose disappear, the liquid becomes strongly charged with oxalic acid, and this, as well as the formic and acetic acids, is finally resolved into carbonic anhydride and carbonic oxide, so that the solution at last contains nothing but sulphuric acid.

*Electrolysis of Glycol.*—Hydrogen was evolved at the negative pole, and at the positive pole a gaseous mixture containing  $CO_2$ , 5.00;  $CO$ , 57.15;  $O$ , 37.85. The current was interrupted at the end of 36 hours. The liquid, saturated with calcium carbonate and distilled, gave a distillate containing trioxymethylene, whilst the residue in the retort contained calcium formate and calcium glycolate, some unaltered glycol, and a glucose identical with that obtained by the electrolysis of glycerol.

*Electrolysis of Mannitol.*—Hydrogen was evolved at the negative pole, and at the positive pole a gaseous mixture containing  $CO_2$ , 22.1;  $CO$ , 55.0;  $O$ , 22.9. The liquid treated as in the glycol experiment, gave trioxymethylene, calcium formate, and the calcium salt of a new acid. This calcium salt, when separated from the accompanying calcium formate, purified, and analysed, gave numbers corresponding with the formula  $C_6H_8CaO_8 + 2H_2O$ . It is very soluble in water, and it is not precipitated either by lime water, or by lead acetate or subacetate. It reduces silver nitrate almost instantaneously, without heating, and in the dark; if the mixture be heated slightly a metallic mirror is obtained. At 120° C., the calcium salt loses 6—7 per cent. of water, and at 150° it swells up, and begins to decompose. The acid, obtained from the calcium salt by decomposition with oxalic acid, is a syrupy product, forming very soluble, gummy salts, with barium,

lead, and magnesium. The author assigns the formula  $C_6H_8O_8$  to this acid, and suggests that it may be an aldehyde of saccharic acid,  $C_6H_{10}O_8$ , bearing the same relation to the latter that glyoxylic (or glyoxalic) acid,  $C_2H_2O_3$ , does to glycollic acid,  $C_2H_4O_3$ . A glucose identical with that obtained from glycerol, and probably also with the mannitol of Gornp-Besanez, was also formed during the electrolysis, together with a considerable quantity of oxalic acid, but no saccharic acid or mannitolic acid could be detected.

*Electrolysis of Glucose.*—Hydrogen was evolved at the negative pole, and at the positive pole a gaseous mixture containing  $CO_2$ , 22.8;  $CO$ , 18.2;  $O$ , 59.0. The electrolysed liquid contained trioxymethylene, formic acid, and saccharic acid.

*Electrolysis of Alcohols when the Electrodes are separated by a Porous Partition.*—In these experiments, the liquids to be electrolysed were contained in a porous cell, into which the positive electrode was introduced, the porous cell being surrounded with acidulated water, into which the negative electrode was plunged. The alcohols experimented with were methyl alcohol, ethyl alcohol, and glycerol. The products were the same as in the experiment in which no porous partition was employed.

*Electrolysis of Acetic Acid.*—25 c.c. of glacial acetic acid was mixed with 40 c.c. of water, acidulated with one-tenth of sulphuric acid, and submitted to the action of the current from 4 Bunsen cells. At the end of three hours the gaseous mixture evolved at the positive pole contained  $CO_2$ , 41.3;  $CO$ , 11.4;  $O$ , 47.3. After 24 hours the gas evolved consisted of  $CO_2$ , 45.4;  $CO$ , 9.2;  $O$ , 45.4. The proportion of carbonic anhydride was still greater at the end of 36 hours. After 48 hours the liquid was examined, and found to contain formic acid, but no oxalic acid.

*Electrolysis of Oxalic Acid.*—The sole products in this case were carbonic anhydride and carbonic oxide. The gaseous mixture evolved at the positive pole contained about 50 per cent.  $CO_2$ , and 10 per cent.  $CO$ , the rest being oxygen. At the end of 48 hours all the oxalic acid had disappeared.

*Electrolysis of Formic Acid.*—The sole products were carbonic anhydride and carbonic oxide. If concentrated formic acid is used, carbonic anhydride is the only product.

*Electrolysis of Alcohols in presence of Phosphoric Acid.*—Experiments were made with solutions of methyl alcohol, ethyl alcohol, glycerol, and glycol, acidulated with phosphoric instead of sulphuric acid. A larger proportion of phosphoric acid than of sulphuric acid was found necessary, in order to secure the decomposition of the alcohols, but the products were exactly the same, and in about the same proportions as when sulphuric acid was used, except that in the case of methyl and ethyl alcohols no hydrogen methyl or ethyl phosphate was formed.

*Action of Ozonised Oxygen on the Alcohols.*—The action of ozonised oxygen on the alcohols is very slow; for example, when a stream of this gas is passed through solutions of glycerol, glucose, or mannitol, the escaping gas is still strongly odorous, and the liquid contains only very small quantities of acetic or formic acid, even after many days' action. Carbon dioxide and carbon monoxide are also formed. Contrary to

expectation, ozone was found to act much more quickly on the alcohols of low atomicity, such as methyl and ethyl alcohols, than on the polyatomic alcohols, glycol, glycerol, mannitol, and glucose. The action of electrolytic oxygen is similar to that of ozone in this respect.

*Action of Hydrogen Peroxide on the Alcohols.*—Hydrogen peroxide appears to have no action on the alcohols, whether in acid, neutral, or alkaline solutions, dilute or concentrated, even after the lapse of several days.

The author concludes that the products obtained in the electrolytic experiments above described are not due to direct electrolysis of the alcohols, but are simply due to the action on the alcohols of the oxygen, resulting from the electrolysis of the acidulated water. He suggests the electrolytic method as a convenient one for effecting the oxidation of organic bodies at a low temperature, and in a manner permitting the examination of intermediate products.

J. M. H. M.

**Two New Hydrofluoboric Acids and Ethylene Fluoboric Acid.** By F. LANDOLPH (*Ber.*, 12, 1583—1586).—When boric fluoride acts on amylene, the latter is polymerised, and a fluoboric acid,  $\text{Bo}_2\text{O} \cdot \text{H}_3\text{HFl}$ , is obtained. It is a clear yellow liquid boiling at  $160^\circ$ , is easily decomposed by water, forming boric acid. A second fluoboric acid,  $\text{Bo}_2\text{O}_2\text{H}_2\text{HFl}$ , is obtained when boric fluoride acts on anethol at high temperatures. It is a heavy, transparent liquid, boiling at  $130^\circ$ . Like the above it fumes in contact with air, and is decomposed by water.

*Ethylene fluoboric acid*,  $\text{C}_2\text{H}_4\text{HFl} \cdot \text{BoO}_2$ , is formed by the action of boric fluoride on ethylene at  $25\text{--}30^\circ$  in sunlight. It is a clear, mobile, fuming liquid (b. p.  $124\text{--}125^\circ$ ), of sp. gr. 1.0478 at  $23^\circ$ . It burns with a green flame. Water decomposes this compound, forming boric acid, and a volatile compound (b. p.  $10\text{--}15^\circ$ ), which does not burn with a green flame, and is supposed to be ethyl fluoride.

P. P. B.

**Sulphates of Mono- and Poly-hydric Alcohols and Carbohydrates.** By P. CLAESSON (*Ber.*, 12, 1719—1721).—*Methyl sulphate* is best prepared by the decomposition at  $130\text{--}140^\circ$  of hydrogen methyl sulphate obtained by the action of sulphuric monochloride on methyl alcohol.

*Ethyl sulphate* is an oily liquid insoluble in water (b. p.  $208^\circ$ ).

The polyhydric alcohols when treated with sulphuric monochloride yield the corresponding hydrogen sulphates.

Dextrose, dextrin, starch, and cellulose, form with sulphuric monochloride *dextrochloride-tetrasulphonic acid*,  $\text{C}_6\text{H}_5(\text{SO}_3\text{OH})_4 \cdot \text{CHCl} \cdot \text{ClHO}$ , which crystallises in large prisms. Corresponding compounds could not be obtained with levulose and galactose.

W. C. W.

**Changes of Ammonium Isethionate at High Temperatures.** By F. CARL (*Ber.*, 12, 1604—1607).—Ammonium isethionate heated at  $210\text{--}220^\circ$  loses 12 per cent. of its weight, forming a body which crystallises from alcohol in leaflets, having a pearly lustre (m. p.  $196\text{--}198^\circ$ ).—Seyberth (*Ber.*, 7, 391) has observed the same change, but gives  $190\text{--}193^\circ$  as the melting point of the compound produced,

which he describes as an amide of the formula  $C_2H_7NSO_3$ . The author finds this compound has the formula  $C_4H_{13}S_2N_2O_7$ , and explains Seyberth's results by the supposition that his product contained small quantities of another substance, which is formed simultaneously. By boiling with baryta-water, this compound does not form barium isethionate as it would if it were an amide, but a barium salt is formed crystallising in prismatic tables united to globular masses, having the composition  $C_4H_9S_2BaO_7 + H_2O$ . This salt differs from barium isethionate in its action on polarised light, as also in its solubility in alcohol. The author regards the new product as ammonium di-isethionate,  $NH_4SO_3 \cdot (CH_2)_2 \cdot O \cdot (CH_2)_2 \cdot SO_3NH_4$ .

Besides ammonium di-isethionate another body is produced, which is more soluble in alcohol, and has the composition  $C_4H_{13}S_2NO_7$ . It owes its existence to the evolution of ammonia observed when ammonium isethionate is heated. That it is not an acid salt is shown by the fact that when treated with alcoholic ammonia, and the solution evaporated on the water-bath, the solution has still an acid reaction. For this reason the author attributes to this compound the formula  $NH_4SO_3 \cdot (CH_2)_2 \cdot SO_3 \cdot (CH_2)_2 \cdot OH$ .  
P. P. B.

**Epichlorhydrin-Derivatives.** By M. BRESLAUER (*J. pr. Chem.* [2], 20, 188—193).—Von Richter (*Ber.*, 10, 677) observed that dry sodium acetate has no action on epichlorhydrin, but that in presence of absolute alcohol, ethyl acetate and epihydrin alcohol (glycide) are formed. The author confirms von Gegerfelt's statement (*Bull. Soc. Chim.*, 23, 160), that epihydrin acetate,  $C_3H_5OAc$ , is produced by the action of potassium acetate on epichlorhydrin. The best mode of preparing this acetate is to heat equivalent proportions of epichlorhydrin and potassium acetate in a flask provided with an upright condenser at 110—115° for several hours, and then raise the temperature slowly to 150°. By extracting the product with ether, *epihydrin acetate* (b. p. 164—168°) is obtained, and also a liquid boiling at 258—261°, which Gegerfelt regarded as glycerol-triacetin, but which is really a polymeride of epihydrin acetate.

Epihydrin acetate is a mobile liquid (sp. gr. 1.129 at 20°), soluble in alcohol and ether. It precipitates metallic silver from an ammoniacal solution of silver nitrate. By the action of potash on epihydrin acetate diluted with ethyl acetate, glycerol is produced, but if soda is used instead of potash *epihydrin alcohol*,  $C_3H_5O.OH$ , is obtained. The alcohol boils at 160°, and is soluble in water, alcohol, and ether. When heated with water glycerol is formed.

Diglycid,  $(C_3H_5O.OH)_2$ , results from the saponification of the polymeric modification of epihydrin acetate.  
W. O. W.

**Sugar from Populin.** By E. O. v. LIPPMANN (*Ber.*, 12, 1648—1649). When the glucoside populin,  $C_{20}H_{22}O_8 + 2H_2O$ , is decomposed by dilute acids, it splits up into benzoic acid, saliretin,  $C_{14}H_{14}O_8$ , and *grape sugar*.  
W. O. W.

**Partial Synthesis of Milk-sugar, and a Contribution to the Synthesis of Cane-sugar.** By E. DEMOLÉ (*Compt. rend.*, 89, 481).



—Schützenberger (*Ann. Chim. Phys.*, **21**, 235), by the action of acetic anhydride on glucose, obtained an acetyl-derivative of a body formed by the union of 2 mols. of glucose with elimination of water, for which the author proposes the name of *diglucose*. Schützenberger considered this body identical with octacetyl-saccharose. The solubilities of these two ethers in alcohol are, however, different; and octacetyl-saccharose has a specific rotatory power  $[\alpha]_D = 38.36$ , whilst that of octacetyl-diglucose is  $[\alpha]_D = 54.62$ ; moreover, the saccharose-derivative yields saccharose by saponification, whereas the diglucose-compound yields diglucose.

When milk-sugar is heated with a dilute acid, it is converted by assimilation of water into galactose and lactoglucose. When the mixture of these bodies, obtained in the above manner, is dried and heated with acetic anhydride, it is converted into a pitch-like ether, having all the properties of octacetyl-lactose, and giving milk-sugar by treatment with alkalis.

When 2 mols. of glucose, like or unlike, are in presence of a dehydrating agent, they are converted into their anhydrides; and by the action of these anhydrides on acetic anhydride, an ether of a diglucose is formed, just as ethylene oxide takes up acetic anhydride to form an ether of diglycol.

C. W. W.

**Reaction of Tungstates in presence of Mannitol.** By KLEIN (*Compt. rend.*, **89**, 484).—The action of tungstates on mannitol resembles that of borax. A solution of 12 grams mannitol and 4 grams sodium tungstate, made up to 100 c.c., gives a deviation of  $+40'$ . The solution has an alkaline reaction; boiling effects no change.

A solution of 10 grams of mannitol and 4 grams of sodium paratungstate,  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 25\text{H}_2\text{O}$ , made up to 100 c.c., has no rotatory power in the cold, but after boiling produces a deviation of  $+36'$ . The solution, which is originally neutral, becomes strongly acid on boiling.

Barium metatungstate,  $\text{BaW}_6\text{O}_{18} \cdot 9\text{H}_2\text{O}$ , added to a solution of mannitol, produces no deviation, even after boiling. The barium salt is not decomposed by the solution of mannitol, although it is by water alone.

If baryta-water be added to the above solution when boiling, the liquid, after filtering, has a rotatory power of  $+25'$ ; this effect is not produced in the cold.

C. W. W.

**Decomposition of Ethylamine Hydrochloride by Heat.** By M. FILETI and A. RICCINI (*Ber.*, **12**, 1508).—When this salt is heated to a temperature somewhat lower than that at which lead melts, a mixture of ammonia and mono- and di-ethylamine (separated in neutral solution by means of potassium nitrite), ethyl chloride and ethylene is evolved, whilst the residue consists of ammonium chloride, diethylamine hydrochloride, and some undecomposed ethylamine hydrochloride. The reaction is thus analogous to the decomposition of phenylethylamine by heat, except that a further decomposition into ammonia and ethyl chloride takes place.

W. R.

**Cyanethine.** By E. v. MEYER (*J. pr. Chem.* [2], 19, 484—485).—Cyanethine appears to be a tertiary base. When heated with moderately dilute sulphuric or hydrochloric acid at 180—200°, it is transformed into a crystalline base,  $C_6H_{14}N_2O$ , which forms easily soluble and finely crystallising salts.

The investigation is being continued.

A. J. C.

**A Double Function of the Monobasic Acids.** By LOIR (*Ann. Chim. Phys.* [5], 18, 125—138).—In reference to Gerhardt's paper on the anhydrides (*ibid* [3], 37, 333), the author considers that if the anhydrides are classed as ethers, that under certain circumstances the acids may act as alcohols, and if such be the case they must also have the properties of aldehydes. This becomes evident on examination of the formula for acetic acid, which may be written thus  $\cdot OH \cdot CH_2 \cdot COH$ . Considered as an alcohol it is  $C_2H_5O(HO)$ , the  $C_2H_5O$  containing an aldehyde grouping  $CH_2 \cdot COH$ . The following experiments are adduced in support of this view.

By the action of reducing agents on aldehydes, alcohols are obtained, and when acids are treated with hydriodic acid, Berthelot has shown that the hydrides of the alcohol radicles are formed.

Butyric acid (b. p. 155—160°) when heated with a concentrated solution of sodium hydrogen sulphite at 0°, yields long transparent needles; these melt at 20° without the evolution of sulphurous anhydride, whilst butyric acid floats on the top of the solution. On collecting the crystals, dissolving in water, and distilling with sulphuric acid, sulphurous anhydride is evolved, and butyric acid distils over. Butyric acid decolorises potassium permanganate, and reduces ammoniated silver solutions. Valeric acid has similar properties.

That acetic anhydride possesses the functions of an aldehyde as well as an ether has been shown by the author (this Journal, *Abst.*, 1879, 621). The same holds good for butyric anhydride.

Acetobenzonic anhydride, however, exists in two isomeric modifications, according as it is prepared from sodium benzoate and acetic chloride, in which case the author calls it *acetyl benzoic anhydride*, or from sodium acetate, and benzoic chloride, when it is called *benzoyl-acetic anhydride*. The two bodies have the same chemical properties, except in their reaction with hydrochloric acid.

*Benzoyl-acetic anhydride* when heated in hydrochloric acid gas boils at 130°, and acetic chloride comes over, leaving benzoic acid as a crystalline residue.

*Acetyl-benzoic anhydride* when treated in a similar manner boils at 160°, and benzoic chloride distils over.

With chlorine similar results are obtained, the residue in the first case being *chlorobenzoic acid*, and in the second *chloroacetic acid*.

These two isomeric bodies may be considered as ethereal salts; benzoyl acetic anhydride being the acetic salt of benzoic acid which acts as an alcohol, whilst acetyl benzoic anhydride is the benzoic salt of acetic acid acting as an alcohol.

Benzoic chloride at 0° forms a crystalline compound with sodium hydrogen sulphite.

Since glyoxal and glyoxylic acid are obtained from alcohol by the

action of nitric acid, they may be considered as derivatives of aldehyde and acetic acid. As glyoxal,  $\text{COH.COH}$ , contains the aldehyde-group twice, its mode of formation depends on the previous formation of an alcohol aldehyde; and as we have acetic acid (alcohol),  $\text{OH.CH}_3$ ,  $\text{COH}$ , yielding glyoxylic acid,  $\text{OH.CO.COH}$ , containing the acid and aldehyde groups, it requires the same conditions.

A table showing the relations of the derivatives of alcohol and acetic acids is given. L. T. O'S.

**Existence of Double Salts in Solution.** By P. H. B. INGENHOES (*Ber.*, 12, 1678—1684).—*Darium formionitrate*,  $\text{Ba.NO}_3.\text{CHO}_2 + 2\text{H}_2\text{O}$ , is prepared by dissolving barium nitrate in an almost saturated warm solution of barium formate. Crystals of barium nitrate are first deposited, and then the double salt separates out. Solutions of barium formio-nitrate and aceto-nitrate and calcium acetochloride when dialysed, diffuse like mixtures of simple salts; this shows that these salts dissociate in dilute solutions. W. C. W.

**Oxidising Action of Cupric Oxide; Transformation of Acetic Acid into Glycollic Acid.** By P. CASENEUVE (*Compt. rend.*, 89, 525).—It is known that formic acid is oxidised by cupric oxide to carbonic acid, and similarly, if carbonic acid be regarded as the acid of methylene glycol, it might be expected that acetic acid, the homologue of formic acid, would be oxidised to glycollic acid.

Cupric acetate was heated in a sealed tube with water at  $200^\circ$  for an hour. The tube contained crystallised cuprous oxide, and a liquid which deposited crystals of glycollate of copper. A small quantity of carbonic anhydride was also formed. The reaction is probably expressed by the equation,  $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_4\text{O}_3 + \text{Cu}_2\text{O} + 3\text{C}_2\text{H}_4\text{O}_2$ .

The carbonic anhydride is due to a secondary reaction by which propionic acid is also formed:  $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O} = \text{CO}_2 + \text{C}_2\text{H}_5\text{O}_2 + \text{Cu}_2\text{O} + 2\text{C}_2\text{H}_4\text{O}_2$ : this reaction takes place to a very limited and variable extent. C. W. W.

**Action of Nitric Acid on Epichlorhydrin.** By V. v. RICHTER (*J. pr. Chem.* [2], 20, 193—195).—When epichlorhydrin is treated with 3 or 4 parts of warm nitric acid (sp. gr. 1.38) an energetic reaction takes place. On pouring the acid liquid into water and extracting with ether, *monochlorolactic acid* is obtained. To remove the chloro-nitrohydrin and oxalic acid with which it is mixed, it is dissolved in water, again extracted with ether and converted into the calcium salt. The acid crystallises in flat prisms (m. p.  $77^\circ$ ), which are deliquescent and dissolve readily in alcohol, ether, and water. W. C. W.

**Ethyl Nitracetate.** By FORCRAND (*J. pr. Chem.* [2], 19, 487—488).—This is obtained by the action of silver nitrite on ethyl bromacetate. The product is distilled, and the portion which passes over at  $150^\circ$  (with slight decomposition) is essentially *ethyl nitracetate*, a liquid of sp. gr. 1.133 at  $0^\circ$  (b. p.  $151$ — $152^\circ$ ). By the action of zinc and hydro-

chloric acid it was converted into amido-acetic hydrochloride, whence the silver salt was obtained in iridescent crystals which blacken on exposure to the light.

A. J. C.

**Preparation of Nitrated Fatty Acids.** By J. LEWKOWITSCH (*J. pr. Chem.* [2], 20, 159—173).—Nitro-products could not be obtained by the action of the strongest nitric acid (sp. gr. 1.55) or of a mixture of nitric and sulphuric acids on caproic and stearic acids.

*Ethyl nitroacetate*,  $\text{CH}_3(\text{NO}_2)\text{COOEt}$ , is formed by digesting ethyl iodacetate with silver nitrite at  $100^\circ$ ; towards the end of the process the mixture is heated up to  $130^\circ$ . On treating the product with absolute ether, a pale-yellow liquid, insoluble in water, is obtained, which boils between  $150^\circ$  and  $160^\circ$  with decomposition.

*Ethyl nitropropionate*, prepared by the action of silver nitrite on ethyl  $\beta$ -iodopropionate (which is most readily obtained by heating an alcoholic solution of  $\beta$ -iodopropionic acid with a small quantity of sulphuric acid), is a colourless mobile liquid (b. p.  $161\text{--}165^\circ$ ). The ethyl salt dissolves in a dilute solution of potash; by acidifying the liquid with sulphuric acid and extracting with ether, crystals of nitropropionic acid were in one instance obtained, but the operation generally yields a thick liquid which dries up to a hard glassy mass when exposed over sulphuric acid.

$\beta$ -Nitropropionic acid is easily obtained by adding about 2 equivalents of silver nitrite to 1 of  $\beta$ -iodopropionic acid dissolved in water. (The best results are gained by working with not more than 5 grams of iodopropionic acid for each operation.) The solution of silver nitropropionate which is formed is decomposed by hydrochloric acid and extracted with ether. After evaporating the ethereal solution, a thick liquid remains which solidifies forming a white deliquescent crystalline mass. By recrystallisation from chloroform, the nitro-acid is obtained in pearly-white scales which melt at  $66^\circ$  and decompose at  $160^\circ$ . The acid is soluble in water, alcohol, and ether; its salts are also soluble in water, but undergo decomposition. By reduction with tin and hydrochloric acid,  $\beta$ -nitropropionic acid is converted into  $\beta$ -alanine hydrochloride.

W. C. W.

**Derivatives of Thiocetic Acid.** By S. GABRIEL (*Ber.*, 12, 1639—1641).—*Phenylene-dithiacetic acid*,  $\text{C}_6\text{H}_4(\text{S}\cdot\text{CH}_2\text{COOH})_2$ , is prepared by the action of chloroacetic acid (2 mols.) on a warm alkaline solution of thioresorcinol (1 mol.). On acidifying the mixture with hydrochloric acid, the acid separates out as an oily liquid, which soon solidifies to a crystalline mass. The crystals melt at  $127^\circ$ , forming a turbid liquid which becomes clear at  $150^\circ$ .

*Toluene-dithiacetic acid*,  $\text{C}_6\text{H}_3\text{Me}(\text{S}\cdot\text{CH}_2\text{COOH})_2$ , obtained by a similar reaction, crystallises in needles (m. p.  $151\text{--}5^\circ$ ), soluble in hot water.

*Phenylene-dioxyacetic acid*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\text{COOH})_2$ , produced by the action of chloroacetic acid on an alkaline solution of resorcinol, forms pale-yellow crystals (m. p.  $193^\circ$ ). *Dibromophenylene-dioxyacetic acid*, separates out as a white powder when bromine vapour is passed into the aqueous solution of this acid. It is deposited from a hot alcoholic

solution in white, silky needles (m. p.  $250^{\circ}$ ). *Benzyl-thiacetic acid*,  $C_6H_5.CH_2.S.CH_2.COOH$ , crystallises in flat plates (m. p.  $59^{\circ}$ ). The *amide*,  $C_6H_5.CH_2.S.CH_2.CONH_2$ , is obtained in rectangular plates (m. p.  $97^{\circ}$ ), by the action of ammonia at  $100^{\circ}$  on ethyl benzyl-thi-acetate (b. p.  $275-290^{\circ}$ ). W. C. W.

**Lauric Acid and its Conversion into Undecylic Acid.** By F. KRAFFT (*Ber.*, 12, 1664—1668).—Lauric acid is best prepared from commercial bay oil (*Ol. laurin unguinos*). For this purpose the oil is saponified by boiling with a solution of potash for several hours; the potash soap is decomposed by warm hydrochloric acid, and the mixture of acids thus set free is distilled under greatly diminished pressure. The first portion of the distillate subjected to repeated redistillation under diminished pressure yields pure lauric acid (m. p.  $43.5^{\circ}$ , b. p.  $222.5^{\circ}$  under 100 mm. pressure).

The *ketone*,  $C_{13}H_{26}O$ , obtained by the dry distillation of a mixture of barium laurate and acetate under diminished pressure, melts at  $28^{\circ}$  and boils at  $263^{\circ}$ . On oxidation with chromic mixture this substance yields acetic acid and an oily liquid consisting of a mixture of undecylic acid and unaltered ketone. The undecylic acid is converted into its barium salt, which is treated with ether to remove the ketone. This acid crystallises in scales, which melt at  $28.5^{\circ}$  and boil at  $213^{\circ}$  under 100 mm. pressure. W. C. W.

**Tridecylic, Pentadecic, and Margaric Acids.** By F. KRAFFT (*Ber.*, 12, 1668—1675).—Myristic acid, prepared by the saponification of Muscata butter and purified by distillation under diminished pressure, melts at  $53.5^{\circ}$  and boils at  $248^{\circ}$  under 100 mm. pressure.

The ketone,  $C_{15}H_{30}O$ , obtained by the dry distillation under diminished pressure of a mixture of barium acetate and myristate, melts at  $39^{\circ}$ , boils at  $294^{\circ}$ , and on oxidation yields acetic and tridecoic acids.

The latter acid, purified by redistillation and conversion into its barium salt, melts at  $40.5^{\circ}$  and boils at  $236^{\circ}$  under 100 mm. pressure.

By a similar process *pentadecic acid*,  $C_{17}H_{34}O_2$ , can be obtained from palmitic acid (m. p.  $62^{\circ}$  and b. p.  $268.5^{\circ}$  under 100 mm. pressure). The ketone melts at  $48^{\circ}$  and boils at  $320^{\circ}$ . Pentadecic acid melts at  $51^{\circ}$ , and boils at  $257^{\circ}$  under 100 mm. pressure.

*Margaric acid*, prepared synthetically from stearic acid (b. p.  $287^{\circ}$  under 100 mm. pressure), is identical with the margaric acid obtained by Heintz (*Pogg. Ann.*, 102, 257) by the saponification of cetyl cyanide. The acid melts at  $59.8^{\circ}$  (uncorr.), and boils at  $277^{\circ}$  under 100 mm. pressure.

The discovery of tridecoic and pentadecic acids makes the list of fatty acids complete as far as stearic acid. W. C. W.

**Hydroxyethylmethylacetic Acid.** By W. v. MILLER (*Ber.*, 12, 1544).—To show that Neubauer's angelic acid resulted from ethyl-methylacetic acid, which, together with isobutylic formic acid, is a product of the oxidation of amyl alcohol obtained by fermentation, the author

prepared ethylmethylacetic acid by Sauer's process, and oxidised it with potassium permanganate. The product was  $\alpha$ -hydroxyethylmethylacetic acid,  $\text{C}(\text{EtMe})(\text{OH})\text{COOH}$  (m. p.  $68^\circ$ ). On distilling this acid with sulphuric acid no methylcrotonic acid was formed.

W. R.

**Hydroxisobutylformic Acid.** By W. v. MILLER (*Ber.*, 12, 1542—1543).—From a careful comparison of the copper salts, the author concludes that the dimethacrylic acid, prepared by him by oxidising  $\beta$ -hydroxisobutylformic acid,  $\text{CMe}_2(\text{OH})\text{CH}_2\text{COOH}$ , is identical with an acid obtained by A. and M. Saytzeff, by oxidising synthetically prepared allyl dimethyl carbinol. The  $\beta$ -hydroxisobutylformic acid, of which the formula is given above, is an intermediate product between isobutylformic acid and its ultimate product of oxidation with potassium permanganate, viz., dimethacrylic acid. W. R.

**Synthesis of Ketonic Acids.** By P. HOFFERICHTER (*J. pr. Chem.* [2], 20, 195—200).—*Trichloroacetic cyanide*, prepared by the action of silver cyanide on trichloroacetic bromide, is a colourless liquid (b. p.  $117$ — $119^\circ$ ), soluble in ether. It refracts light powerfully, and has a sp. gr.  $1.559$  at  $15^\circ$ . It is decomposed by water with formation of hydrocyanic and trichloroacetic acids. On exposure to moist air, a deliquescent white crystalline substance is formed. A solid polymeride, which is produced in small quantities in the preparation of the liquid trichloroacetic cyanide, crystallises in rhombic plates (m. p.  $140^\circ$ ), soluble in alcohol and in ether. It is decomposed on boiling with water.

*Trichloroacetylcarboxylic acid* is formed when the liquid cyanide is treated with dilute hydrochloric acid (sp. gr.  $1.16$ ) at  $50^\circ$ . It is separated from trichloroacetic acid by recrystallisation of the sodium salts. Sodium trichloroacetylcarboxylate crystallises in prisms containing 2 mols.  $\text{H}_2\text{O}$ , which are less soluble than the tabular crystals of sodium trichloroacetate. The acid forms small prisms (m. p.  $89^\circ$ ), soluble in water. By the action of fuming hydrochloric acid on trichloroacetic cyanide, a white crystalline amide is produced, which appears to have the composition  $\text{C}_3\text{Cl}_5\text{O}_5\text{H}_5\text{N}_2$ . W. C. W.

**Maleic Acid from Dichloroacetic Acid.** By S. TANATAR (*Ber.*, 12, 1563—1566).—Ethyl dichloroacetate dissolved in alcohol is not acted on by molecular silver at the boiling point of alcohol; if, however, ethyl dichloroacetate is heated with molecular silver at  $210^\circ$  in sealed tubes, silver chloride is formed, and a small quantity of an ethereal salt boiling about  $210^\circ$ , which on saponification with baryta-water yields barium maleate.

Sodium acts energetically on dry ethyl dichloroacetate; if the reaction is modified by use of anhydrous ether, there is found amongst the products of decomposition, an ethereal salt distilling between  $100$ — $120^\circ$ , which is more soluble in water than the ethyl dichloroacetate; it is soluble in warm baryta-water. On standing, this solution decomposes with formation of barium carbonate. The nature of this product is as yet unexplained.

P. P. B.

**Occurrence of Tricarballic and Aconitic Acids in Beet-Juice.** By E. O. VON LIPPMANN (*Ber.*, 12, 1649—1651).—Tricarballic acid is not found in fresh beetroot, but the author confirms his previous observation (*Ber.*, 11, 707, this Journal, 1878, Abst., 662) as to the occurrence of the calcium salt of this acid in the vacuum pans of the beet-sugar manufactory. Aconitic acid, detected by Behr in the juice of the sugar-cane (*Ber.*, 10, 351, this Journal, 1877, 2, 182) is also present in beet-juice. W. C. W.

**The Acid of *Drosera Intermedia*.** By G. STEIN (*Ber.*, 12, 1603).—According to Lucas and Trommsdorf (*Annalen*, 8, 237) the acid contained in this plant is malic, whilst Reess and Will (*Central-blatt f. Agriculturchemie*, 10, 230) suppose it to contain formic, propionic, and butyric acids, and finally Hager asserts that it contains citric and malic acids. The author has extracted some of this acid, and from the characters of its salts concludes that it is citric acid. The acid has also been obtained crystallising in rhombic prisms, and the analysis of its lead salt shows it to be citric acid. P. P. B.

**Derivatives of Triethyl citrate.** By J. CONEN (*Ber.*, 12, 1653—1655).—*Triethyl citrate*,  $C_6H_5OH(COOEt)_3$ , prepared by the action of hydrochloric acid on a mixture of citric acid and alcohol, is a thick colourless liquid, sp. gr. 1.1369 at 20° compared with water at 4°, b. p. 261° under 300 mm. pressure.

*Tetrethyl citrate*,  $C_6H_4OEt(COOEt)_3$ , is formed when the product of the action of sodium on triethyl citrate (diluted with dry ether) is heated with ethyl iodide at 100°. This citrate is a pale-yellow oil, sp. gr. 1.1022 at 20°, boiling at 290° with decomposition.

A liquid having the composition  $C_6H_5(COOEt)_3$ , and of sp. gr. 1.1064, is produced by heating a mixture of phosphorus chloride and ethyl citrate at 100°. This substance decomposes on distillation.

W. C. W.

**Action of Phosphorus Pentachloride and Hydriodic Acid on Saccharic Acid.** By H. DE LA MOTTE (*Ber.*, 12, 1571—1573).—The results published by C. J. Bell (this Journal, Abst., 1879, 917) are the same as those published by the author in his Dissertation (Halle, 1878). The author also points out that chloromucic acid obtained from saccharic or mucic acid always crystallises with 2 mols. of water of crystallisation,  $C_6H_4Cl_2O_4 \cdot 2H_2O$ .

Saccharic acid when heated with hydriodic acid and amorphous phosphorus in sealed tubes at 140—150°, yields a small quantity of an acid, m. p. 148—149°, the analysis of which, and its properties, as also those of its salts, show it to be adipic acid. P. P. B.

**Constitution of Deoxalic Acid.** By J. KLEIN (*J. pr. Chem.* [2], 20, 146—159).—By acting on ethyl oxalate with sodium-amalgam, Löwig, in 1861, obtained a substance of the formula  $C_{11}H_{16}O_8$ , which he regarded as the triethyl salt of deoxalic acid,  $C_6H_4O_8$ , and by heating this with dilute sulphuric acid, he converted it into ethyl racemate, with evolution of carbonic anhydride. Brunner, in 1870, contended

that the original reduction-product of ethyl oxalate has the formula  $C_{12}H_{20}O_8$ , and is the triethyl salt of an acid of the formula  $C_4H_5O_8$ , which, however, he could not isolate, owing to its decomposition into racemic and glyoxylic acids. The author has confirmed Löwig's results in the following manner:—Ethyl deoxalate prepared by the action of sodium-amalgam on ethyl oxalate melts at  $85^\circ$ , and has all the properties attributed to it by Löwig. The barium salt was prepared by titrating the ethyl salt with standard baryta-water. Both the titration and the analysis of the barium salt point to the correctness of Löwig's formula. The calcium salt has the formula  $(C_4H_5O_8)_2Ca_2$ . The free acid, prepared from the barium salt by means of sulphuric acid, forms very deliquescent crystals, and from several analyses appears to have the formula  $C_4H_5O_8 \cdot H_2O$ .

Treated with acetic or with benzoic chloride, it forms monacetyl- and benzoyl-deoxalic acid, and with acetic anhydride, or with benzoic chloride, at a higher temperature, a diacetyl or dibenzoyl acid. It appears therefore to contain two alcoholic hydroxyls. The amount of carbonic anhydride evolved on boiling the acid with dilute sulphuric acid was estimated, and agreed with the equation  $C_4H_5O_8 \cdot Et_3 = C_4H_5O_6 \cdot Et_3 + CO_2$ , ethyl racemate being formed at the same time. The ethyl racemate gave an acid agreeing with the ordinary racemic acid in all its properties.

On heating deoxalic acid with hydriodic acid no reduction took place, but it was converted into racemic acid, and at a still higher temperature, succinic acid was produced. The tricarboxylic acid, of which deoxalic acid is a hydroxylic derivative, was not isolated in this reaction.

W. R.

**Synthesis of the Closed Benzene Ring.** By V. v. RICHTER (*J. pr. Chem.* [2], 19, 205—208.—In order to accomplish the synthesis of benzene by means of diethylene-diketone the author subjected the succinates of potassium, sodium, magnesium, calcium, and lead to dry distillation. The distillate contained quinol, and benzene was obtained by the action of zinc dust on the distillate, but diethylene-diketone has not yet been isolated.

No benzene derivatives were formed by distilling ethylene succinate with zinc dust.

W. C. W.

**Derivatives of Isodurene.** By M. BIELEFELD (*Annalen*, 198, 380—388).—The isodurene used in these experiments was prepared by the method described by Jannasch (*Ber.*, 8, 355), viz., by the action of sodium on a mixture of monobromomesitylene and methyl iodide diluted with a small quantity of benzene. Isodurene boils at  $195$ — $197^\circ$ . *Isodurenesulphonic acid* obtained by treating the hydrocarbon with fuming sulphuric acid crystallises in plates which melt in their water of crystallisation at  $100^\circ$ . *Lead isodurenesulphate*,  $(C_8H_7Me_3SO_3)_2Pb + 3H_2O$ , forms needle-shaped crystals, so also do the salts of *barium* (anhydrous), *calcium* ( $3H_2O$ ), and *potassium* ( $1H_2O$ ). The *copper salt* crystallises in pale bluish-green needles, which are anhydrous. The *silver salt* forms transparent rhombic plates; the *strontium salt* is deposited in lustrous plates containing



9 mols.  $\text{H}_2\text{O}$ . The *sodium salt* crystallises in shining rhombic plates containing  $\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ . The *cobalt salt* crystallises in pale red four-sided plates which contain  $7\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ .

When isodurene is boiled with dilute nitric acid (1 : 4) for two days, a mixture of  $\alpha$ - and  $\beta$ -isoduric acids ( $\text{C}_{10}\text{H}_{12}\text{O}_2$ ) is formed, together with a polybasic acid, which does not melt at  $300^\circ$ , and also several nitro-products. The  $\alpha$ - and  $\beta$ -acids can be separated by recrystallisation from hot water, or by fractional crystallisation of their calcium salts.

$\alpha$ -Isoduric acid melts at  $215^\circ$  and at a higher temperature sublimes, forming long glistening needles. It is very sparingly soluble in water, but dissolves in alcohol, ether, and hot benzene. From a dilute ethereal solution, the acid is deposited in clear monoclinic crystals which refract light powerfully. The  $\alpha$ -acid can be distilled in a current of steam. Its salts are crystalline and are soluble in water.  $(\text{C}_{10}\text{H}_{11}\text{O}_2)_2\text{Ca} + 5\text{H}_2\text{O}$ ,  $(\text{C}_{10}\text{H}_{11}\text{O}_2)_2\text{Sr} + 5\text{H}_2\text{O}$ , and  $(\text{C}_{10}\text{H}_{11}\text{O}_2)_2\text{Ba} + 4\text{H}_2\text{O}$  form needle-shaped crystals.

$\beta$ -Isoduric acid is much more soluble in water, ether, chloroform, benzene, alcohol, and light petroleum than the  $\alpha$ -acid. It crystallises in needles which melt at  $120$ — $123^\circ$ . The calcium salt forms glistening needle-shaped crystals containing 2 mols.  $\text{H}_2\text{O}$ .

Monobromisodurene boils at  $252$ — $254^\circ$ , and crystallises in nacreous plates. W. C. W.

**Behaviour of Cymene in the Animal Organism.** By JACOBSEN (*Der.*, 12, 1512—1518).—As cymene has been prepared from normal propyl iodide and parabromotoluene, and as the author has shown that the hydrocarbon produced from parabromocumene and methyl iodide is not cymene, but an isomeride, no doubt would remain regarding the constitution of cymene were it not for two reactions. The first of these, noticed by Kraut and confirmed by the author, is that cymene is produced by the action of zinc dust on cymyl alcohol, and the second is the oxidation of cymene in the organism to cuminic acid, observed by Nencki and Ziegler. Both of these results are unfavourable to the theory that cymene contains a normal propyl group. In the present paper, the author gives an account of a repetition of Nencki and Ziegler's experiments.

The cymene was administered to a dog, and its urine, after evaporation, was acidified and shaken with ether. After distilling off the ether, the residue gave a copious precipitate with hydrochloric acid, which was found to consist for the most part of cuminuric acid,  $\text{C}_{11}\text{H}_{14}\text{NO}_2$ . The filtrate from this precipitate gave a distillate containing a little paraxylylic acid, showing that the cymene administered to the dog had contained a little pseudocumene.

Cuminuric acid melts at  $168^\circ$ , and volatilises without decomposition. It is almost insoluble in cold, but comparatively easily soluble in warm water; it dissolves with the greatest readiness in alcohol; ether, however, dissolves it with difficulty. From water it crystallises—(1), on addition of an acid, in nacreous scales; and (2), on slow evaporation, in large iridescent rhombic plates, without water of crystallisation; and from alcohol, on evaporation, in radiated crystals.

The *barium salt*,  $(C_{12}H_{14}NO_2)_2 \cdot H_2O$ , dissolves with some difficulty, and crystallises from its hot solution in long right-angled plates or in flat needles, arranged in a fan-shaped form. The *calcium salt*,  $(C_{12}H_{14}NO_2)_2 \cdot 3H_2O$ , crystallises in thin needles, and is also soluble with difficulty. The *ammonium* and *potassium salts* are very easily soluble, and crystallise in needles. The two latter salts give precipitates with salts of zinc, manganese, cadmium, magnesium, ferrous and ferric salts, copper, lead, and silver; with mercuric chloride, it gives no precipitate, and with mercuric nitrate, a flocculent insoluble precipitate.

This cuminic acid probably differs from that which Cahours prepared from cuminic chloride and glycolyl silver.

In order further to confirm the relations of this acid, it was decomposed by heating with hydrochloric acid; it split up into glycocine and cuminic acid, melting at  $116-117^\circ$ , and agreeing in all its properties with that described by others. It thus appears that cuminic acid is really a product of oxidation of cymene in the animal organism, but to remove all doubt, and further to connect cuminic and cuminic acids, the latter acid was synthetically prepared from cymyl alcohol and glyccol silver. The product was identical in all respects with that separated from the urine.

If, then, there is conclusive proof that cumene contains normal propyl and that cuminic acid contains isopropyl, then the preparation of cumene from cymyl alcohol with zinc dust involves the transformation of isopropyl into normal propyl, and, on the other hand, the formation of cuminic acid from cymene implies the opposite change.

In conclusion, the author draws attention to the fact that in his experiments, the chief product was cuminic acid, whilst in those of Nencki and Ziegler, cuminic acid was formed. He also found the latter acid, but in very small amount.

W. R.

**Products of Distillation of Gum-ammoniac Resin with Zinc-dust.** By G. L. CIAMICIAN (*Ber.*, 12, 1658—1664).—The only liquid which is obtained by the distillation of gum-ammoniac resin with zinc-dust consists of a mixture of para- and metaxylene (b. p.  $136-138^\circ$ ), meta-ethyltoluene (b. p.  $160^\circ$ ), methyl ortho-ethylphenate (b. p.  $180-200^\circ$ ), and a hydrocarbon having the composition  $C_{12}H_{20}O$ , which yields on oxidation benzoic, acetic, and perhaps propionic acids. No naphthalene derivatives are formed. Ortho-ethylphenol obtained by the saponification of the methyl ether is a thick, colourless oil (b. p.  $220^\circ$ ), which remains liquid when cooled down in a freezing mixture. On fusion with potash, it is decomposed with production of salicylic acid.

W. C. W.

**Condensation-products of Aldehydes with Primary Aromatic Bases.** By O. FISCHER (*Ber.*, 12, 1693—1694).—Although the author was unable to obtain *diamidotriphenylmethane* by decomposing tetramethyldiamidotriphenylmethane with concentrated hydrochloric acid, he has succeeded in preparing it by the action of zinc chloride on a mixture of aniline and benzaldehyde. This base is a crystalline substance and is soluble in light petroleum. By the action of methyl

iodide, at 130°, on the solution of the base in methyl alcohol, tetramethyldiamidotriphenylmethane methiodide is produced.

W. C. W.

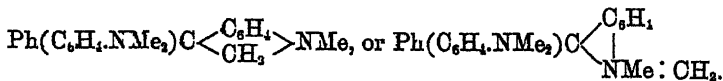
**Condensation-products of Tertiary Aromatic Bases.** By O. FISCHER (*Ber.*, 12, 1685—1693).—A good mode of preparing *tetramethyldiamidotriphenylmethane* consists in digesting on a water-bath a mixture of benzaldehyde (1 mol.) and dimethylaniline (2 mols.) with a quantity of solid zinc chloride, equal in weight to the dimethylaniline taken, until scarcely any dimethylaniline separates out on the addition of an alkali to a small quantity of the product. If the mass grows very thick during the operation, sufficient water should be added to reduce it to a pasty consistency. The solution obtained by treating the crude product with boiling water deposits the base in a state of comparative purity. The *hydrochloride*,  $C_{23}H_{24}N_2 \cdot 2HCl$ , crystallises out in colourless hygroscopic needles, when ether is added to a solution of the base dissolved in strong hydrochloric acid mixed with alcohol. The *methiodide*,  $C_{23}H_{23}N_2 \cdot 2MeI$ , is deposited from concentrated aqueous solutions in plates, and from dilute solutions in needles, which melt at 218—222° with decomposition into methiodide and the original base.

*Tetramethyldiamidotriphenylcarbinol*,  $C_{23}H_{24}N_2 \cdot H_2O$ , the base contained in benzaldehyde green, is obtained in colourless needles by recrystallising from light petroleum the precipitate formed by the action of an alkali on the salts produced by the oxidation of the leuco-base.

The crystals melt at 120°, and form ethers when recrystallised from alcohol. The *ethyl ether*, best prepared by heating the carbinol with alcohol at 110°, melts at 162°.

The *zincochloride*,  $C_{23}H_{24}N_2 + ZnCl_2 + H_2O$ , crystallises in dark-green glistening needles or scales freely soluble in water. The *sulphate*,  $C_{23}H_{24}N_2 + H_2SO_4$ , forms beetle-green needles, containing 1 mol. of water. The *methiodide*,  $C_{23}H_{23}OCH_2N_2(MeI)_2 + 2H_2O$ , crystallises in colourless needles, which begin to decompose at 100°.

The constitution of benzaldehyde green (*Ber.*, 12, 796; and this *Journal*, 1879, *Abst.*, 787) is represented by one of the following formulæ:—



*Tetramethyldiamidopropyltriphenylmethane*, obtained from cumic aldehyde and dimethylaniline, crystallises in long colourless needles (m. p. 118°). It bears close resemblance to the leuco-base of benzaldehyde green, yielding on oxidation a bluish-green colouring matter.

Dimethylaniline and methylal yield tetramethyldiamidodiphenylmethane (m. p. 91°), which has been previously described by Hanhart (*Ber.*, 12, 681; this *Journal*, 1879, *Abst.*, 714. Doebner (*Ber.*, 12, 810), and by Michler and Moro (*ibid.*, 12, 1170). The compound which Pauly (*Annalen*, 187, 198) obtained by the action of benzo-

phenone chloride on dimethylaniline has the composition  $C_{21}H_{21}N$ , and not  $C_{21}H_{19}N$  as given by the discoverer.

Dimethylaniline-phthalein,  $C_{24}H_{24}N_2O_2$ , is prepared by the action of zinc chloride on a mixture of phthalic chloride and dimethylaniline. The excess of dimethylaniline is removed from the resulting product by treatment with hot water, and the residue is dissolved in dilute acetic acid. The precipitate which is thrown down on the addition of an alkali to this acid liquid is dried and dissolved in a small quantity of benzene. When light petroleum is poured into this solution, the impurities separate out, together with a portion of the phthalein. On evaporating the filtrate, the phthalein slowly crystallises out, and is purified by recrystallisation from benzene. The pure substance forms colourless rhombohedrons, which melt at  $188^\circ$ . A green colouring matter is produced as a bye-product in the preparation of dimethylaniline-phthalein; its formation increases with the temperature at which the process is conducted.

W. C. W.

**Some New Colouring Matters.** By P. GREIFF (*Ber.*, 12, 1610—1611).—By the action of chloranil on dimethylaniline, a deep bluish-violet colouring matter is obtained; it is insoluble in water, but dissolves in alcohol and acetic acid. Methylidiphenylamine gives a colouring matter of a deeper blue. These reactions take place at the ordinary temperature, and give good yields. Quinone gives similar products. Chloranilic acid and the sulpho-acids of chloranil react differently. Phenanthraquinone gives under similar circumstances bluish-violet bodies, having strongly marked dichroism. The addition of zinc chloride in all these reactions is advantageous.

P. P. B.

**Action of Hydrocyanic Acid on Diazo-compounds.** By S. GABRIEL (*Ber.*, 12, 1637—1639).—A substance, having the composition  $C_8H_8N_4$ , separates out in orange-coloured crystals when a cold aqueous solution of diazobenzenesulphate or nitrate is allowed to drop slowly into a well-cooled solution of potassium cyanide. The crystals are dissolved in a small quantity of warm alcohol, and warm water is added to the solution. When the mixture cools, large prisms (m. p.  $69^\circ$ ) are deposited, which decompose, forming a brown resin, if left in contact with the mother-liquor for several hours. The compound is also decomposed by boiling in water, hydrocyanic acid being evolved, and a resinous body formed.

By the action of potassium cyanide on bromodiazobenzene nitrate (from bromaniline, m. p. 61) an unstable crystalline product (m. p.  $127.5^\circ$ ) is obtained, which appears to have the composition  $C_8H_5BrN_4$ .

By a similar reaction, the compound  $C_8H_8N_4$  may be prepared from toluene. It is deposited from an alcoholic solution in reddish-yellow plates or needles, which melt at  $77.5^\circ$ , but decompose if heated at  $60^\circ$  for some time.

W. C. W.

**Formula of Quinhydrone.** By H. WICHELHAUS (*Ber.*, 12, 1500—1505).—The question considered in this paper is which one of the following formulæ for quinhydrone is the correct one:—



proposed by Graebe, or  $\text{HO.C}_6\text{H}_4\text{O.OO.C}_6\text{H}_4\text{O.OO.C}_6\text{H}_4\text{OH} = \text{C}_{20}\text{H}_{10}\text{O}_6$ , suggested by the author.

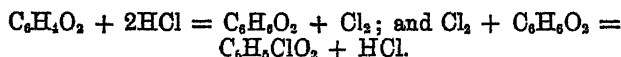
Nietzki's argument in favour of the former formula is, that as quinone is reduced to quinol in theoretical proportion by sulphurous acid, quinhydrone should also be acted on in the same manner. In support of this view, he has adduced a series of experiments, in which quinhydrone was reduced by such a quantity of sulphurous acid as to lead to the formula  $\text{C}_{12}\text{H}_{10}\text{O}_4$ .

The author has repeated these experiments, and has found that they are untrustworthy, owing to the fugitive blue colour produced by iodine in presence of quinhydrone during titration of excess of sulphurous acid.

He next brings forward in support of his own views, the fact that methylquinhydrone, prepared by melting at  $100^\circ$  a mixture of methylquinol with quinone, gives numbers which, though differing but slightly from those required for Graebe's formula, still agree better with the formula proposed by him; also, that during the reaction between methylquinol and quinone, hydrogen is set free, which reduces the latter, giving rise to a considerable formation of quinol; and, lastly, that on decomposing methylquinhydrone with sulphurous acid, the resulting quinol bears to the methylquinol the proportion of 1 : 2.5. This agrees closely with the proportion calculated for  $\text{C}_{20}\text{H}_{15}\text{O}_6$ , viz., 1 : 2.26, but not with that for  $\text{C}_{12}\text{H}_{12}\text{O}_4$ , viz., 1 : 1.13.

In further support of his views, the author calls attention to the fact that dimethyl- and diethyl-quinone have no action on quinol, for hydroxyl is not present in their molecules. When substituted quinols act on quinone, unsubstituted quinhydrone is invariably formed, whilst a reduction takes place owing to the liberated hydrogen.

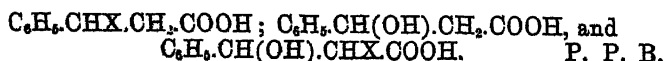
In a similar manner the formation of chloroquinol by treatment of quinone with hydrochloric acid is explicable by the following equations:—



An analogous reaction takes place with hydrobromic acid. The resulting monobromoquinol has the formula  $\text{C}_6\text{H}_5\text{BrO}_2$ ; it may be sublimed in small quantities, melts at  $110$ — $112^\circ$ , and is soluble in chloroform, benzene, and hot water. During its purification by crystallisation from light petroleum, a product, agreeing fairly with the formula  $\text{C}_6\text{H}_4\text{Br}_2\text{O}$ , is obtained less soluble than the former; it crystallises in white needles grouped in stars, and melts at  $185$ — $186^\circ$ .

W. R.

**Constitution of Phenylhalogenpropionic Acids.** By E. ERLENMEYER (*Ber.*, 12, 1607—1610). The author criticises the views held by Glaser (*Annalen*, 154, 167) and Fittig (*ibid.*, 195, 170) on the constitution of the phenylhalogenpropionic acids and phenyllactic acids prepared by them, and concludes that these acids have the following constitutions:—



**Monobromocinnamic Acids and Phenylfumaric Acid.** By F. BARISCH (*J. pr. Chem.* [2], 20, 173—188).—By the action of alcoholic potash on dibromohydrocinnamic acid, Glaser (*Annalen*, 143, 330) obtained two isomeric monobromocinnamic acids, which were separated by recrystallising their ammonium salts.  $\beta$ -Bromostyrene,  $\text{PhCBr} : \text{CH}_2$  (b. p.  $117^\circ$ ), is formed as a bye-product in this operation from the decomposition of a portion of the monobromocinnamic acid (m. p.  $131^\circ$ ),  $\text{PhCBr} : \text{CH}.\text{COOH}$ .

Glaser prefixes  $\alpha$  to the acid crystallising in needles (m. p.  $131^\circ$ ), and calls the isomide which forms crystalline plates (m. p.  $120^\circ$ ) the  $\beta$ -acid. The author proposes to reverse this nomenclature, since  $\alpha$ -derivatives have a lower melting point, and enter more readily into reactions than  $\beta$ -compounds. Both  $\alpha$ - and  $\beta$ -monobromocinnamic acid when treated with alcoholic potash yield the same phenylpropionic acid,  $\text{PhC} : \text{C}.\text{COOH}$ . When hydrochloric acid is passed through their alcoholic solutions, they both yield the same ethyl  $\beta$ -bromocinnamate (b. p.  $290^\circ$ ). The  $\alpha$ -acid during the act of etherification is transformed into the  $\beta$ -acid.

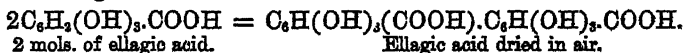
*Phenylfumaric acid*,  $\text{C}_{10}\text{H}_8\text{O}_4$ , or  $\text{COOH}.\text{CPh} : \text{CH}.\text{COOH}$ , is obtained by heating at  $150^\circ$  a mixture of potassium cyanide, alcohol, and ethyl- $\beta$ -bromocinnamate, and boiling the product with alcoholic potash. On the addition of hydrochloric acid, a resinous substance separates out, the supernatant liquid is concentrated by evaporation and extracted with ether, when the new acid is obtained in white crystals (m. p.  $161^\circ$ ), freely soluble in alcohol, ether, and hot water. The potassium, sodium, ammonium, calcium, and barium salts of this acid dissolve readily in water. W. C. W.

**Formation of Para-hydroxybenzoic Acid from Sodium Phenate.** By H. OST (*J. pr. Chem.* [2] 20, 208).—Very small quantities of para-hydroxybenzoic acid and traces of  $\alpha$ -phenol-dicarboxylic acid are formed by the action of carbonic anhydride on sodium phenate. The presence of these acids can be detected in the filtrate after the precipitation of the salicylic acid. W. C. W.

**Constitution of Ellagic Acid.** By H. SCHIFF (*Ber.*, 12, 1533—1537).—Gallic acid, when boiled with arsenic anhydride, forms digallic acid by union of two molecules. If the mass is dried and heated to  $160^\circ$ , the arsenic acid is reduced and ellagic acid is formed:—

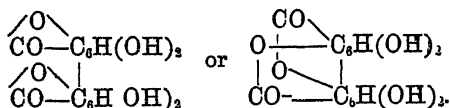


The question is, are the two benzene-groups in ellagic acid united directly, or by means of oxygen? The ease with which that acid is formed from gallic acid seems to point to a negative answer; but, on the other hand, no attempt to convert ellagic into gallic acid has been successful. Assuming that direct union subsists, the author suggests the following formulæ:—



Ellagic anhydride cannot be etherified, does not combine with hydrogen, and cannot be reconverted into gallic or tannic acids; it forms a

tetracetyl derivative. The author supposes it to have one of the following formulæ:—



The two molecules of water are not expelled at the same temperature, but it has recently been shown that the temperature at which the second is expelled is much lower than was formerly supposed. These formulæ sufficiently represent the neutral and basic salts formed by ellagic acid.

W. R.

**New Organic Acid occurring in Agaricus Integer.** By W. THÖNER (*Ber.*, 12, 1635—1637).—From 19 to 20 per cent. of mannitol can be extracted from *Agaricus integer* by treatment with boiling alcohol. An acid having the composition  $\text{C}_{18}\text{H}_{20}\text{O}_2$  is contained in the alcoholic mother-liquors. In order to isolate it, the alcoholic solution is evaporated to dryness on a water-bath, the residue is exhausted first with water to remove any mannitol which may be present, and then with hydrochloric acid. It is finally dissolved in a solution of soda to which one-third of its volume of alcohol has been added. After evaporating off the alcohol, the acid is precipitated by boiling with dilute hydrochloric acid. The pure acid is deposited from an alcoholic solution in white needles (m. p.  $70^\circ$ ) soluble in ether, benzene, toluene, carbon bisulphide, chloroform, boiling alcohol, and boiling glacial acetic acid. The potassium, sodium, and ammonium salts are sparingly soluble in cold water, but dissolve in warm dilute alcohol.  $\text{Ba}(\text{C}_{18}\text{H}_{20}\text{O}_2)_2$ , and  $\text{Pb}(\text{C}_{18}\text{H}_{20}\text{O}_2)_2$ , and also the calcium, magnesium, and silver salts are white insoluble compounds. The lead salt melts at  $114^\circ$ .

W. C. W.

**Kynuric Acid.** By M. KRETSCHY (*Ber.*, 12, 1673—1675).—Kynuric acid is completely resolved into its elements by fusion with potash. Chinoline is formed when this acid is heated at  $240^\circ$  with strong hydrochloric acid, and also when it is distilled with zinc-dust.

W. C. W.

**Aromatic Thiocarbamides.** By C. FEUERLEIN (*Ber.*, 12, 1602—1603).—The preparation of phenylcyanamide from monophenyl thiocarbamide has been described in a former communication (this Journal, Abst., 1879, 804). From analysis, its formula is  $(\text{NH} : \text{C} : \text{NPh})_2 + 3\text{H}_2\text{O}$ ; when placed over sulphuric acid, it forms a syrupy mass, which on standing becomes crystalline, forming phenylcyanamide. The platinum,  $(\text{NH} : \text{C} : \text{NPhHCl})_2\text{PtCl}_4$ , and the silver compounds,  $(\text{NH} : \text{C} : \text{NPh})_2\text{Ag}$ , have been obtained. Monophenyl thiocarbamide is converted into monophenylguanidine,  $\text{NH}_2\text{C}(\text{NH})_2\text{Ph}$ , by the action of alcoholic ammonia. This compound when heated burns without previously melting, and is decomposed by exposure to the air or over sulphuric acid into phenylcyanamide.

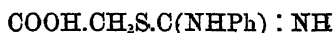
P. P. B.

**Formulæ of Thiohydantoins.** By C. LIEBERMANN and A. LANGE (*Ber.*, 12, 1588—1595).—One of the authors has already described

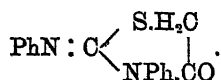
the preparation of diphenylthiohydantoin (this Journal, Abst., 1879, 651), which when decomposed with alcoholic potash was supposed to yield diphenyl thiocarbamide, potassium sulphide, and potassium glycollate. Further investigation has shown that this decomposition yields thioglycollic acid, a reaction also observed by Andreasch (*Ber.*, 12, 1385). This decomposition is expressed thus:  $C_{16}H_{12}N_2SO + KOH + H_2O = C_{16}H_{12}N_2O + C_2H_3KSO_2$ . Diphenyl-thiohydantoin is similarly decomposed by alcoholic ammonia at  $150^\circ$ , forming aniline and thioglycollic acid, thus:  $C_{16}H_{12}N_2SO + 3NH_3 + 4H_2O = 2C_6H_7N + C_2H_3SO_2NH_4 + CO_2(NH_4)_2$ .

The supposition that thioglycollic acid owes its formation to a secondary reaction, is found to be untenable, since glycollic acid cannot be converted into this thio-acid either by boiling with potassium hydrogen sulphide or with diphenylthiocarbamide and alcoholic potash. Further, the product  $C_6H_7NSO_2$  obtained from diphenylthiocarbamide (*loc. cit.*) is also resolved by alcoholic potash and baryta-water into carbanilide, carbonic anhydride, and thioglycollic acid. These results

show that the formula,  $CS \begin{smallmatrix} \swarrow NPh-CH_2 \\ \searrow NPh-CO \end{smallmatrix}$ , attributed to diphenylthiohydantoin is incorrect. Rather must it be regarded as analogous to Jäger's phenylcarbodiimido-thiacetic acid,

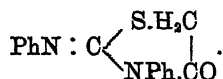


(*J. pr. Chem.* [2], 16, 17), and therefore its formula is



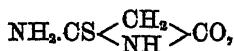
Its formation may then be explained as follows:—

- (1.)  $CS(NHPh)_2 + ClC_2H_3O_2 = ClC(NHPh)_2.S.CH_2.COOH$ .
- (2.)  $ClC(NHPh)_2.S.CH_2.COOH - HCl - H_2O =$

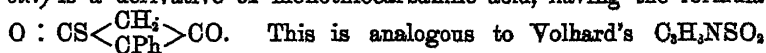


This view of the constitution of the thiohydantoin is supported by the investigations of Wallach (this Journal, 36, 312), Wallach and Bleibtren (*Ber.*, 12, 1061), Bernthsen (*Annalen*, 197, 341), and the investigation on thiocarbamide of Claus (*Ber.*, 7, 236 and 841).

In this light thiohydantoin will have the formula—



and the product obtained by Lange from diphenylthiohydantoin (*loc. cit.*) is a derivative of monothiocarbanilic acid, having the formula



This is analogous to Volhard's  $C_6H_5NSO_2$  (*J. pr. Chem.*, 9, 8), which may be written  $O:CS \begin{smallmatrix} \swarrow CH_2 \\ \searrow NH \end{smallmatrix} > CO$ . In



an analogous manner Nencki's compounds (*J. pr. Chem.* [2], 16, 1) has the constitution  $S : CS < \begin{smallmatrix} CH_2 \\ NH \end{smallmatrix} > CO$ , and to the carbaminethiacetic acid of the same author, the formula  $O : C(NH_2)S.CH_2COOH$  may be attributed.

These new formulæ also explain why it is so difficult to remove the sulphur from thiohydantoins, a fact which has been pointed out by Volhard (*Annalen*, 166, 384), Mulder (*Ber.*, 8, 1264), Maly (*Annalen*, 168, 133), and noticed by the authors in the case of diphenylthiohydantoin.

P. P. B.

**Action of Potassium Pyrosulphate on Indigo-white.** By A. BAETTER (*Ber.*, 12, 1600—1602).—According to Baumann, the indican contained in urine is not a glucoside, but the potassium salt of a sulphonic acid of indoxyl (*Zeit. f. Physiol. Chem.*, 1, 60; *Die Synthetischen Prozesse in Thierkörper*, Berlin, 1878, 6; R. Baumann and L. Brieger, *Zeit. f. Physiol. Chem.*, 3, 254; and Baumann and Tiemann, this Journal, Abst., 1879, 936). A body possessing the same properties as the above-mentioned indican is obtained by heating 1 part of indigo, 1 of ferrous sulphate, 2 of potash, 2 of water, and 3—4 of potassium pyrosulphate in sealed tubes for 12 hours at 60°. From this, the author concludes that the indican from urine is potassium hydrindigotin-sulphonate,  $C_{16}H_{10}N_2(O.SO_3K)_2$ . Baumann's analyses confirm this observation.

P. P. B.

**Action of Chlorine on Dibenzyl.** By R. KADE (*J. pr. Chem.* [2], 19, 461—467).—*Paradichlorodibenzyl*,  $C_6H_4Cl.CH_2.CH_2.C_6H_4Cl$  (m. p. 112°), is formed by passing chlorine over the crystalline product obtained by melting together iodine and dibenzyl, and continuing the action until hydrochloric acid begins to be evolved. The resulting thick cherry-coloured oil is distilled, and the crystals of paradichlorodibenzyl deposited from the oily distillate are purified by crystallisation from alcohol. It forms thin fine laminæ, closely resembling naphthalene, and is easily soluble in alcohol, ether, and chloroform.

It can be sublimed, giving an odour of bitter almonds when heated, and be distilled without decomposition. It yields parachlorobenzoic acid by oxidation with chromic mixture.

The oily body which is formed at the same time is probably monochlorodibenzyl.

Quite a different reaction takes place when chlorine is passed into a mixture of pulverised dibenzyl with iodine. In this case toluylene with unaltered dibenzyl is produced. Toluylene is also formed to some extent by the action of chlorine on the vapour of dibenzyl, and by passing chlorine into melted dibenzyl until it begins to turn brown, and then distilling, the whole is transformed into toluylene. Continuing the action until hydrochloric acid is again given off, dichlorotoluylene,  $C_7H_7Cl_2$  (m. p. 170°) is obtained. It crystallises in silky white needles or laminæ, and easily dissolves in alcohol and ether.

Toluylene is also formed from dibenzyl by the action of potassium chlorate and hydrochloric acid. It can be distilled and sublimed like

benzoic acid. Its alcoholic solution gives a red coloration with ferric chloride.

A. J. C.

**Derivatives of  $\eta$ -Dichloronaphthalene,  $\delta$ -Nitronaphthalenesulphonic Acid.** By P. T. CLEVE (*Ber.*, 12, 1714).— $\alpha$ -Trichloronaphthalene (m. p.  $65^\circ$ ) was prepared by the action of phosphorus pentachloride on  $\eta$ -dichloronaphthalene (m. p.  $48^\circ$ ). The salts of  $\delta$ -nitronaphthalenesulphonic acid are crystalline. The chloride of this acid melts at  $169^\circ$ , the amide at  $216^\circ$ , and the ethyl salt at  $108^\circ$ .

W. C. W.

**Action of Chlorine on Chloronaphthalene: Nitro-derivatives of  $\alpha$ - and  $\beta$ -Dichloronaphthalene.** By O. WIDMANN (*Ber.*, 12, 1714—1715).— $\alpha$ -Monochloronaphthalene combines with chlorine to form  $C_{10}H_7Cl_2$  (m. p.  $67^\circ$ ), and  $C_{10}H_7Cl.Cl_2$  (m. p.  $131.5^\circ$ ), whilst  $\beta$ -monochloronaphthalene forms a liquid trichloronaphthalene, and a tetrachloride,  $C_{10}H_5Cl_4$  (m. p.  $81^\circ$ ), which when treated with potash gives a trichloronaphthalene, melting at  $140^\circ$ . By the action of chlorine on an acetic acid solution of  $\alpha$ -monochloronaphthalene, an aceto-chloride,  $C_{10}H_6Cl_2.Cl_2OAc$  (m. p.  $195^\circ$ ) is produced.  $\alpha$ -Dichloronaphthalene yields only one nitro-derivative, viz., the trinitro (m. p.  $178^\circ$ ), but the  $\beta$ -compound forms a mono- and a dinitro-derivative, which melt at  $92^\circ$  and  $158^\circ$  respectively.

W. C. W.

**On the Quinone occurring in *Agaricus Atrotomentosus*.** By W. THÖRNER (*Ber.*, 12, 1630—1635).—The spectrum of the red alcoholic solution of the quinone extracted from *Agaricus atrotomentosus* by means of ether is characterised by a deep red band between B and D.

A crystalline ammonium salt separates out as a dirty green-coloured powder, when strong ammonia is added to a hot alcoholic solution of the quinone. It dissolves in dilute alcohol and in water, forming a violet solution, which produces coloured precipitates with many metallic salts, viz., a flesh-coloured crystalline precipitate with barium chloride; dirty pink flocculent precipitate with calcium chloride; brownish-green with lead acetate; black with ferric chloride; dark green with mercuric chloride; brownish-black with alum; reddish-brown with copper sulphate; brown with platinum chloride; dirty green with silver nitrate; and a beautiful green crystalline precipitate with magnesium sulphate.

The compound obtained by the action of benzoic anhydride on the quinone forms yellow needle-shaped crystals, which melt at  $285^\circ$  with decomposition. By heating the quinone with dilute nitric acid, oxalic and nitric acids and also a nitro-product are formed. The latter body is a yellow powder (m. p.  $255$ — $260^\circ$ ) soluble in alcohol and chloroform.

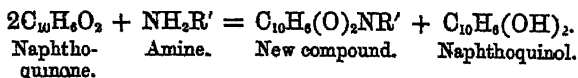
By the reduction of the quinone with hydriodic acid, or by zinc and hydrochloric acid, two bodies are produced, viz., a yellow powder, insoluble in the usual solvents, but easily converted into quinone by alkalis, and a white crystalline compound (m. p.  $162$ — $164^\circ$ ), soluble in alcohol and ether.

When heated with zinc-dust, a large volume of gas is evolved, but no solid hydrocarbons were formed in appreciable quantity. From these results, the author concludes that this substance is methylidihydroxynaphthoquinone,  $C_{10}H_8Me(O_2)(OH)_2$ .

The mother-liquor from the quinone contains an acid (m. p.  $54^\circ$ ), which dissolves in benzene, toluene, ether, chloroform, carbon bisulphide, glacial acetic acid, and petroleum ether. Its barium, calcium, lead, and silver salts are insoluble in water. W. C. W.

**Action of Ammonia and Amines on Quinones.** By T. ZINCKE *Ber.*, 12, 1641—1647).—*Phenanthrenequinonimide*,  $C_{14}H_8O.NH$  (m. p.  $159^\circ$ ) is obtained in yellow, needle-shaped crystals, by passing gaseous ammonia into a warm alcoholic solution of the quinone, or by dissolving the quinone in warm concentrated alcoholic ammonia,  $C_{14}H_8O_2 + NH_3 = C_{14}H_8O.NH + H_2O$ . The imide is decomposed by boiling with alcohol, the quinone being regenerated. It combines with acids to produce red-coloured compounds, which are destroyed by water, with production of the quinone. When heated with acetic or benzoic anhydride, the imide loses a molecule of water, giving rise to a crystalline compound (m. p.  $247^\circ$ ) which is sparingly soluble in hot benzene. By the prolonged action of alcoholic ammonia on phenanthrenequinone, the imide which is first formed disappears, and a mixture of a basic substance soluble in acetic acid, and a neutral compound insoluble in acetic acid, is produced. The latter compound sublimes in lustrous yellow needles, which have the composition  $C_{28}H_{16}N_2$ . A second basic substance, very soluble in alcohol, is also formed. It is probably identical with von Sommaruga's base (*Ber.*, 12, 982). A yellow crystalline compound, probably  $C_{14}H_8O.NMe$ , separates out, when phenanthrenequinone is treated with an alcoholic solution of methylamine. The crystals are insoluble in alcohol, but dissolve in hot benzene. They form a blue compound with strong hydrochloric acid.

The mother-liquor from the yellow compound contains a strong base,  $C_{16}H_{14}N_2$ , which appears to be formed according to the following equation:  $C_{16}H_8O_2 + 2MeNH_2 = C_{16}H_8(NMe)_2 + 2H_2O$ . This substance crystallises in colourless prisms (m. p.  $186^\circ$ ), and forms well crystallised salts, viz., the *hydrochloride*  $C_{16}H_{14}N_2.HCl$ , colourless prisms, soluble in water, insoluble in alcohol; the *nitrates*, fine needles, sparingly soluble in water and in alcohol; the *sulphates*, needles sparingly soluble in alcohol; the *oxalates*, transparent prisms, soluble in hot dilute alcohol. *Naphthoquinone* forms with ammonia a brown amorphous product, but with primary amines it yields crystalline derivatives, according to the equation:—



The compound  $C_{16}H_{14}O_2.NPh$  is obtained by adding an excess of aniline to a hot alcoholic solution of naphthoquinone. The precipitate which is thrown down on the addition of water to the mixture is treated with acetic acid to remove excess of aniline, and is then recrystallised from alcohol, when the pure substance separates out in

lustrous red needles, which melt at  $191^{\circ}$ , and sublime at a higher temperature. The crystals dissolve in hot benzene, alcohol, and ether; they yield with sulphuric acid a red solution, and with alcoholic potash a purple colour.

By the action of zinc and hydrochloric acid, or of sulphurous acid, the compound is split up into naphthoquinol and aniline.

With paratoluidine, naphthoquinone forms a beautiful red compound, crystallising in needles (m. p.  $200^{\circ}$ ). The methylamine compound crystallises in bright red needles, which melt at  $225^{\circ}$ , and the ethylamine compound forms orange-coloured needles (m. p.  $140^{\circ}$ ).

A crystalline substance is also produced by the action of diphenylamine on naphthoquinone, in presence of hydrochloric acid.

Benzoquinone differs from naphthoquinone in its behaviour to amines, e.g.,  $2C_6H_4O_2 + 2Ph.NH_2 = C_6H_4O_2(NHPh)_2 + C_6H_4(OH)_2$ .

W. C. W.

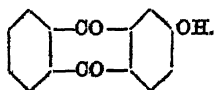
**Amidoanthraquinone from Anthraquinone-monosulphonic Acid.** By H. R. v. PERGER (*Ber.*, 12, 1566—1571).—Anthraquinone-monosulphonic acid, or its ammonium salt, when heated with ammonia in sealed tubes at  $190^{\circ}$ , yields a red crystalline product, which is soluble in concentrated hydrochloric acid, and on addition of water is thrown down again as an orange or red flocculent precipitate. By repeated sublimation in a current of carbonic anhydride, and crystallisation from alcohol and benzene, this compound is obtained pure. Analysis shows it to be monamidoanthraquinone,  $C_{14}H_7O_2.NH_2$  (m. p.  $302^{\circ}$ ); and its formation may be expressed thus:  $C_{14}H_7O_2SO_3NH_4 + (NH_3)_2 = C_{14}H_7O_2.NH_2 + (NH_4)_2SO_3$ . Bourcart (*Ber.*, 12, 1418) describes a compound obtained in the same way, which melts at  $301^{\circ}$ , and to which he attributes the formula  $C_{14}H_6O_2.NH_2.OH$ ; such an amidoanthraquinol should be soluble in alkalis, which is not the case with this compound. The views of the author are further supported by the behaviour of this compound with nitrous acid; first a yellow crystalline body is obtained (m. p.  $238^{\circ}$ ), which on boiling with alcohol yields anthraquinone; and on boiling with water,  $\alpha$ -monoxanthraquinone is obtained.

Heated with acetic anhydride amidoanthraquinone yields the yellow acetoxy-derivative,  $C_{14}H_7O_2.NHAc$ ; it is soluble in alcohol and ether. It melts at  $257^{\circ}$ , the melting-point of Bourcart's (*loc. cit.*) acetoxy-derivative, to which he attributes the formula  $C_{14}H_6O_2.NAc_3$ .

In conclusion, the author states that attempts made to prepare mononitroanthraquinone according to Böttger and Petersen's method (*Annalen*, 166, 147) have given negative results.

P. P. B.

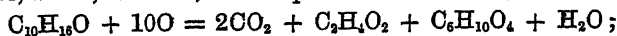
**Decomposition of Hydroxyanthraquinone by Potash.** By C. LIEBERMANN and J. DEHNST (*Ber.*, 12, 1597).—Amongst the products obtained by the fusion of anthraquinone-monosulphonic acid with potash, the authors found small quantities of paraoxybenzoic acid. This owes its existence to the decomposition of monhydroxyanthraquinone, which may, therefore, have the constitutional formula—



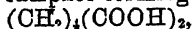
**Constitution of Camphor-compounds.** By M. BALLO (*Ber.*, 12, 1597—1600).—In another communication (*Annalen*, 197, 321) the author has given his reasons for regarding camphor as a tertiary alcohol, having the constitution

$$\begin{array}{c} \text{HC} : \text{C}(\text{CH}_3) - \text{CH}_2 \\ | \\ (\text{OH})\text{C} : \text{C}(\text{C}_3\text{H}_7) - \text{CH}_2 \end{array}$$

This view is supported by the fact that when camphor is oxidised by boiling chromic mixture, acetic, carbonic, and adipic acids are formed, thus:



the central nucleus of the camphor forming adipic acid,



the methyl group, carbonic acid, whilst the propyl group forms carbonic acid and acetic acid.

The author regards camphrene,  $\text{C}_9\text{H}_{14}\text{O}$ , as a homologue of camphor, since it also yields adipic acid when oxidised (Kachler, *Annalen*, 164, 90), and has the properties of an alcohol.

P. P. B.

**Essence of Marjoram.** By BRUYLANTS (*J. Pharm.* [4], 30, 33—35).—Essence of marjoram, obtained by distilling the flowery tops of *Origanum Marjorana* in a current of steam, is a yellowish liquid, when freshly prepared (sp. gr. 0.911 at 15°), but becomes brown on standing. It has a pungent smell, and a hot, peppery, and slightly bitter taste. It is dextrorotatory, and has an acid reaction. When distilled, it begins to boil at 185°, but the temperature rapidly rises to 200°, and remains constant between 215 to 220°, a resinous mass being left in the retort.

By repeatedly fractioning the oil which passes over at 185—190°, a portion is obtained, boiling between 160—162°, consisting principally of a terpene.

The fraction boiling at 215—220° yields no portion having a constant boiling point, nor does it deposit crystals when cooled to -25°. Its vapour-density and analysis correspond with either laurel camphor or borneol. When distilled with phosphoric anhydride, it yields a mixture of cymene and a terpene (b. p. 160—170°). When treated with acetic anhydride, it forms a compound (b. p. 230—235°), which with alcoholic potash yields terpene and potassic acetate. Chromic mixture oxidises it with the formation of acetic and formic acids, and laurel camphor.

Essence of marjoram is therefore composed of a dextrorotatory hydrocarbon, 5 per cent.; a mixture of dextrorotatory camphor and borneol, 85 per cent.; resin, 10 per cent.

L. T. O'S.

**Essences of Lavender and Spike.** By BRUYLANTS (*J. Pharm.* [4], 30, 139—141).—Essence of lavender when freshly prepared is a colourless liquid, which becomes yellow on standing; it smells of lavender, and its taste is hot, camphorous, and slightly bitter. It is levorotatory, has an acid reaction, and sp. gr. 0.875 at 15°. It begins to boil at 185°, the temperature quickly rises to 190°, and the greater portion distils over between 195—215°. The first portion of the distillate consists of a mixture of acetic and formic acids, but contains no valeric acid. By repeated fractionation, a levorotatory ter-

perene (b. p.  $162^{\circ}$ ) is separated, capable of forming a crystalline hydrochloride. The essence also contains a mixture of camphor and borneol: this mixture forms an acetate (b. p.  $230^{\circ}$ ), which is decomposed by potash, yielding a terpene and potassium acetate. When it is distilled with phosphoric anhydride, a hydrocarbon is obtained, consisting for the most part of terpene, and containing also some cymene. Essence of lavender consists of terpene, 25; borneol ( $\frac{1}{3}$ ), and camphor ( $\frac{1}{3}$ ), 65; resin, 10 per cent.

*Essence of Spike.*—This essence obtained from *Lavandula aspiculata* is a colourless liquid, which in time thickens and darkens in colour. It has an acid reaction, and sp. gr. 0.9081 at  $15^{\circ}$ . Its odour resembles that of lavender. Its composition is almost identical with that of essence of lavender, but as it contains more hydrocarbon, it begins to boil at  $170$ — $175^{\circ}$ . It is laevorotatory. Its composition is as follows:—Terpene, 35; borneol and camphor, 55; resin, 10 per cent.  
L. T. O'S.

**Limited Oxidation of the Essential Oils. Part V. The Atmospheric Oxidation of Turpentine.** By C. T. KINGZETT (*Chem. News*, 39, 279).—The author has shown in his previous papers that when so-called essential oils are exposed to the atmosphere, peroxide of hydrogen is indirectly produced. In turpentine oil, it appears as if a camphoric peroxide,  $C_{10}H_{14}O_4$ , is first formed, and that in contact with water this is decomposed, yielding hydrogen peroxide and camphoric acid, thus:  $C_{10}H_{14}O_4 + 2H_2O = C_{10}H_{16}O_4 + H_2O_2$ .

Similarly, terpene,  $C_{10}H_{16}$ , and menthene,  $C_{10}H_{18}$ , give rise to peroxide of hydrogen, whilst hydrocarbons of the formula  $C_{15}H_{24}$  do not.

As all terpenes and menthene yield cymene,  $C_{10}H_{16}$ , and as cymene itself yields hydrogen peroxide, the author believes that there is some relation between the formation of this body and that of hydrogen peroxide, and this opinion is strengthened by the fact that the hydrocarbon from oil of cloves,  $C_{15}H_{24}$ , yields neither cymene nor hydrogen peroxide.

The product of oxidation which is formed by exposing turpentine to the action of the air, and which in contact with water forms hydrogen peroxide, may be produced in such quantities that when the turpentine oil containing it is heated a little above the boiling point, decomposition occurs with almost explosive violence. The atmospheric oxidation of turpentine is now carried out, on the large scale, in the manufacture of the disinfectant called "sanitas."

Different essential oils and varieties of turpentine absorb oxygen with different degrees of rapidity, and when oxidation has once commenced, the oil absorbs oxygen with increasing rapidity in proportion as the oxidation increases, up to a certain point. As to the differences in this respect in different oils, the author gives the following results deduced from experiment by exposing the various oils under similar conditions to light and air. Assuming that the amount of oxygen absorbed by Russian oil of turpentine (which absorbs the largest amount) be represented by 100, then Swedish oil of turpentine absorbs 100.

|  |      |
|--|------|
| An oil obtained from Switzerland.....        | 89.4 |
| American oil of turpentine.....              | 78.9 |
| Oil of eucalyptus.....                       | 75.0 |
| Adulterated Swedish turpentine .....         | 52.6 |
| " Scotch distilled American turpentine"..... | 42.1 |

The two last-mentioned oils were presumed to be adulterated with so-called pine-oil of commerce. When these oils are placed in cylinders, the mouths of which are covered with papers saturated with a mixture of potassic iodide and starch, the papers become coloured in the order given above, owing to the formation of different quantities of hydrogen peroxide in the vicinity of each.

When the aqueous solution obtained by blowing air through a mixture of turpentine and water ("sanitas"), is evaporated to dryness on a steam-bath, the hydrogen peroxide contained in it is decomposed, the acetic acid is expelled, and there remains a dark coloured matter, which when hot is viscid, and has a sugar-like odour, but on cooling sets to an adhesive but firm mass; when treated with sulphuric acid it gives a colour reaction somewhat resembling that bearing Pettenkofer's name. This adhesive mass, which was slightly volatile at 100°, after drying gave numbers corresponding with the formula  $C_{10}H_{18}O_3$ . It has remarkable antiseptic properties, to which the similar properties of "sanitas" are largely due.

About 95 per cent. of this adhesive matter is soluble in water, forming a yellowish-brown solution, from which charcoal failed to remove the colour, although it absorbed a considerable proportion of the substance itself. This solution on evaporation to dryness left a transparent varnish-like substance, semi-fluid when hot, and volatile at 100°. From analysis, the formula  $C_{10}H_{18}O_3$  was calculated.

The 5 per cent. of the original adhesive substance which was insoluble in water did not give the vivid reaction with sulphuric acid which the soluble portion did; this insoluble matter is soluble in presence of an oily substance which the original aqueous solution contained, and which was expelled on evaporation.

On submitting the soluble portion to distillation, it melted, boiled, and a small quantity of an almost colourless oil passed over, which on cooling became a colourless, soft crystalline mass; this was followed by a permanent oil, which became darker as the distillation proceeded; towards the end, the vapour in the retort had a green colour, and a pitch was left. None of these products have as yet been further examined.

On acidulating the solution of the soluble portion,  $C_{10}H_{18}O_3$ , with dilute sulphuric acid, it becomes milky, and on standing, a slightly coloured oily body separates in considerable quantity. The author hopes that a study of this substance will throw light not only on the constitution of the soluble substance, but also on that of the terpenes as a class.

The aqueous solution ("sanitas") obtained by oxidising Russian turpentine, when neutralised with soda, darkens very much in colour, and on evaporation of the mixture at 100°, a dark soft resin-like residuo is left. On treating this with dilute sulphuric acid, it yields a dark

oily mass: the clear acid solution is filtered and subjected to distillation; as it becomes hot more oil separates out, and an acid distillate passes over, together with 20 or 30 c.c. of a slightly yellow oil with an odour resembling that of mixed cymene and eucalyptus. At the end of the distillation a quantity of tarry-looking matter remains in the retort floating on the acid solution. The acidity of the distillate was found to be due to acetic acid, which amounted to about 0.25 gram per litre of the aqueous solution ("sanitas"), and no other volatile acid could be detected. The author anticipates that the further study of those compounds will be attended with very important and interesting results, inasmuch as they have the advantage of having been produced by the mildest possible oxidation. W. T.

**Fusion of Rhamnetin with Potash.** By L. SMORAWSKI (*Ber.*, 12, 1595—1596).—According to Stein (*Zeit. f. Chem.* [2], 5, 183, 568), rhamnetin when fused with potash yields phloroglucinol and quercetic acid. The author finds that by fusion with potash or soda, rhamnetin is decomposed into phloroglucinol and protocatechuic acid; at the same time, small quantities of a substance are formed which, like quercetic acid, gives a deep red coloration with alkalis. This last-named body could not, however, be obtained in quantities sufficient for analysis. P. P. B.

**Chlorophyll.** By F. HOPPE-SEYLER (*Ber.*, 12, 1555—1556).—When grass-blades, after treatment with ether to remove wax, are cohobated with alcohol, two crystalline colouring matters are dissolved, one of which, named erythrophyll by Bougarel, crystallises out first in greenish-white quadratic tables, whilst the other is more soluble in hot alcohol, and may be purified by crystallisation from ether, from which it is deposited in microscopic needles and scales, dark green by reflected, and brown by transmitted light. The crystals of the latter body are of the consistence of soft wax; it dissolves with difficulty in cold alcohol, easily in hot alcohol, and readily in ether and chloroform. The ethereal and alcoholic solutions of this substance have the known red fluorescence of chlorophyll, and absorb the light between B and C of the spectrum with such intensity, that 1 milligram dissolved in a litre of water gives distinct absorption-bands in a thickness of 3.5 cm., with a Browning's spectroscope. Several analyses show it to have the composition: C, 73.4; H, 9.7; N, 5.62; O, 9.57; P, 1.37; Mg, 0.34 p.c. The presence of phosphorus and magnesium may be due to impurities, and the author proposes to investigate this more closely. He has named this substance *chlorophyllan*, and remarks in conclusion, that it is now possible to estimate the amount of chlorophyll in plants approximately by means of its power of absorbing light. W. R.

**Characin.** By T. L. PHIPSON (*Chem. News*, 40, 86).—Amongst the organic substances present in fresh water is a new and interesting product, to which algae in general owe their peculiar odour, and communicate this odour to the water in which they abound. The author has obtained this substance in minute quantities only at present from *Palmella cruenta*, *Vaucheria terrestris*, and from several *Oscillarias*. It



is apparently more developed in the genus *Charra*, and *C. foetida* will probably yield it in larger quantity than the plants already mentioned.

Characin is a kind of camphor, which is extracted from the above plants in the following manner.

The *Palmella* or *Oscillaria* which is to be treated must be previously dried by exposure to the air, at a temperature not exceeding summer heat, for about 24 hours; it is then covered with cold water in a capsule, which must itself be covered with a sheet of glass, and in the course of about 36 hours more (with *Palmella cruenta*) thin films of characin will be observed floating on the water. The latter is then decanted off into a long tube, together with the films, and shaken up with ether. On evaporation a product is obtained which is quite white, devoid of crystallisation, and more or less unctuous in appearance.

Up to the present time, the author has not obtained this substance in sufficient quantity to ascertain more of its properties D. B.

**Phthalein of Hæmatoxylin.** By E. A. LETTS (*Ber.*, 12, 1651—1653).—*Hæmatoxylin-phthalein*,  $C_{20}H_{30}O_{14}$ , is prepared by heating hæmatoxylin with rather more than half its equivalent of phthalic anhydride at 150—170° for five hours. The alcoholic solution of the crude product is poured into water, when a brown flocculent precipitate separates out, which is filtered, washed, and dried in a vacuum. The phthalein could not be obtained in the crystalline state; when the alcoholic solution is evaporated, it leaves a gummy residue insoluble in water, but soluble in ammonia and soda, with a purple colour. Hæmatoxylin forms white crystalline potassium, sodium, and barium compounds. W. C. W.

**Collidine from Aldehyde.** By A. WISCHNEGRADSKY (*Ber.*, 12, 1506—1508).—The object of this research was to ascertain by oxidation whether collidine,  $C_8H_{11}N$ , is trimethyl-pyridine,  $C_8H_8NMe_3$ , ethyl-methyl-pyridine,  $C_8H_9NMeEt$ , or propyl-pyridine,  $C_8H_9NC_2H_5$ . The collidine was oxidised with chromic acid in presence of sulphuric acid, and yielded an acid crystallising in white slender prisms, soluble with difficulty in cold, but easily soluble in hot water. Its formula was  $C_8H_7NO_4$ , and as it yielded picoline on distillation with lime, it is probably methyl-dicarboxypyridenic acid. From this research, the author believes that collidine may be viewed as trimethyl-pyridine. W. R.

**Piperidine Salts: Quinine Sulphate, and Selenate.** By T. HJORTDAHL (*Ber.*, 12, 1730—1731).—The hydrochlorides and gold double salts of piperidine and methylpiperidine are isomorphous.

Quinine sulphate and selenate are also isomorphous; the relation between the axes of the latter substance is  $a:b:c = 0.9804:1:0.8110$ .

W. C. W.

**Aspidospermine.** By G. FRAUDE (*Ber.*, 12, 1560—1562).—Some account of this alkaloid has already been given by the author (*this Journal*, 1879, *Abst.*, 470). The bark containing it is that of *Aspidosperma quercifolium* (Schlectendahl). Further analyses show aspidospermine to have the composition  $C_{22}N_3O_2$ . Concerning its

preparation, the author finds that the liquors obtained after a precipitation of the alkaloid by means of sodium carbonate yield a further quantity by treatment with phosphotungstic acid. This precipitate is treated with baryta-water, and the solution thus obtained with carbonic acid to precipitate the barium; the alkaloid is then extracted by means of alcohol from the residue left on evaporation. One part of aspidospermine is soluble in 6000 parts of water at  $14^{\circ}$ ; this solution has a bitter taste. It is also soluble in 48 parts of alcohol (99 per cent.) at  $14^{\circ}$ , and in 106 parts of pure ether at the same temperature.

A small quantity of aspidospermine treated with a few drops of concentrated sulphuric acid, and then with a little lead peroxide, gives a cherry-red coloration, which has a violet shade if the alkaloid is not quite pure.

Iodic anhydride and sulphuric acid produce the same reaction, whilst potassium dichromate and sulphuric acid give a brown zone slowly changing to an olive-green. Chlorine reacts on aspidospermine suspended in water, producing a white flocculent mass, which is not dissolved by hydrochloric acid; this compound begins to decompose at  $145^{\circ}$ . Bromine acts similarly.

*Aspidospermine sulphate*,  $(C_{22}H_{30}N_2O_2)_2H_4SO_4$ , is obtained by evaporation and drying at  $120^{\circ}$  as a hard, transparent, resinous mass. The *hydrochloride*,  $3(C_{22}H_{30}N_2O_2 + 4HCl)$ , has similar properties to the sulphate. By treating solutions of the base with potassium chromate the *chromate* is obtained as a yellow precipitate, which on exposure to the air becomes green. The *perchlorate* is obtained by adding aqueous perchloric acid to a not too dilute solution of the base.

Hydrochloric acid solutions of the base are precipitated by potassium mercuric iodide in yellow flocks; by potassium sulphocyanide, as a white flocculent precipitate; by iodine dissolved in potassium iodide, as brown flocks; by picric acid, as a yellow precipitate; and by tannin, as a white precipitate. Further, these solutions reduce Fehling's solution when boiled with it.

According to Penzoldt (*Berl. Klin. Wochenschrift*, 1879, 14), the bark of *Aspidosperma quercifolium* has important medicinal properties. P. P. B.

**Oxidation of Cholic Acid.** By H. TAPPEINER (*Ber.*, 12, 1627—1629).—The author obtained stearic acid as an oxidation-product of cholic acid (*Ber.*, 11, 2258), but Latschinoff denies that this acid is formed (*Ber.*, 10, 2059, and 12, 1022). The discrepancy between these results is explained by the fact that the author employed a mixture of potassium dichromate and sulphuric acid as the oxidising agent, whilst Latschinoff used potassium permanganate.

A weak solution of the oxidising mixture must be used when it is desired to isolate the fatty acids obtained by the oxidation of a small quantity of cholic acid.

A crystalline barium salt,  $(C_{12}H_{13}O_7)_2Ba_2 + 6H_2O$ , is formed by heating a saturated solution of cholic acid in baryta-water in sealed tubes at  $120^{\circ}$ . It crystallises in long white prisms, which are very sparingly soluble in water.

To prepare *pyrocholesteric acid* on the large scale, a solution of cholesteric acid in glycerol is heated at  $198^{\circ}$  for a week; the glycerate is then saponified, and after removing the volatile products by distillation, the pyrocholesteric acid is extracted from the residuum by means of ether.

W. C. W.

**Oxidation-products of Cholic Acid.** By P. LATSCHINOFF (*Ber.*, 12, 1518—1528).—By oxidation of cholic acid, the author did not obtain cholesteric acid, nor fatty acids, as Tappeiner did, but an acid termed choloidic acid, to which Redtenbacher gave the formula  $C_{18}H_{34}O_7$ . This acid, which he prepared by oxidising cholic acid with nitric acid of sp. gr. 1.37, evaporating the oxidised product to dryness, and separating the acid first with alcohol, and then as soluble barium salt, after repeated crystallisation from alcohol, gave numbers agreeing with the formula  $C_{10}H_{16}O_4$ ; it is thus isomeric with camphoric acid, and the author has therefore named it *cholecampphoric acid*.

The properties of cholecampphoric acid are as follows:—It is soluble in water and in ether with difficulty; easily in alcohol, more easily when aqueous, also in acetone, and in acetic acid. From a boiling aqueous solution, it is deposited in such a thick mass of interlaced hair-like crystals, that it presents the appearance of a jelly. It has a bitter, acid, somewhat astringent taste. When heated, it loses water, varying in quantity, but approximating to  $\frac{1}{3}H_2O$ . It does not melt, but begins to blacken at  $270^{\circ}$ . Its solution is dextrorotatory. It is a dibasic acid, forming soluble salts with metals of the alkalis and alkaline earths, and insoluble salts with the heavy metals. The author adduces numerous analyses of the salts to confirm the formula of the acid, and indicates the acid potassium salt,  $C_{10}H_{16}KO_4$ , as a proof of its dibasic character.

Cholecampphoric acid may be regarded as a product of hydration of cholic acid, thus:  $C_{20}H_{38}O_6 + 2H_2O = 2C_{10}H_{16}O_4$ .

Such bodies, and many resembling them, for example cholesterin and cholic acid, may be regarded as compounds of condensed valeryl-enes, and may be connected with the terpenes. Thus cholesterin may provisionally be given the formula  $(C_4H_8)_5H_2O$ , and cholic acid  $(C_5H_8)_5O_2 \cdot \frac{1}{3}H_2O$ . This view is supported by the oxidation of cholic acid into cholecampphoric acid, and also by the results of oxidising cholesterin, the product being trioxycholesterin, analogous to betulin.

W. R.

## Physiological Chemistry.

**Feeding Horses with Fleshmeal.** By DÜNKELBERG (*Bied. Centr.*, 1879, 342—344).—At Dünkelsberg's suggestion, Voigts-Rhetz introduced fleshmeal into the food of the horses of his regiment. The results were very satisfactory, the condition and appetite of the horses becoming much improved. Dünkelsberg states that to every kilogram of dried fleshmeal must be added 5.25 grams chloride of potassium, 27.9 grams phosphate of potassium, and 2.9 grams phosphate of magnesium, in order that the whole of the albumin may be assimilated.

J. K. C.

**Poisoning of Sheep by Lupines.** By H. C. E. SCHULZ, E. WILDT, and others (*Bied. Centr.*, 1879, 344—350).—The disease arises from blood poisoning, caused by paralysis of the urinary and gall-bladder muscles, whereby the constituents of the urine and bile pass into the blood. Schulz has investigated the alkaloids of the lupine, and from experiments on three of them, he finds that they differ very much in their physiological action. No great difference can be observed in the ash of wholesome and injurious lupines, but in some cases the latter contain more alkaloid than the former. There is less alkaloid present in the lupines when in bloom than when fully ripe.

Wildt finds two alkaloids in lupines, of which one is a white crystalline solid, and the other a yellow oily liquid; the latter, according to Schulz, consisting of two different bodies. The crystallised alkaloid appeared quite harmless, but the other had a very poisonous action, producing trembling, violent cramp, diarrhoea, and finally death; but in no case could the same appearances be observed after death as in the case when it has been caused by feeding on lupines. Reports from various sheep farmers go to show that lupines act differently on different sheep, and that when injurious, they have generally been grown on a poor damp soil, or on one which has been sown with lupines for several years previously.

J. K. C.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of Light on the Growth of Plants.** By C. KRAUS (*Bied. Centr.*, 1879, 351).—The alterations of growth produced in plants by absence of light are of two kinds, one part of an organ or plant exhibiting an excessive, whilst another exhibits a diminished growth. This is easily verified in the case of dicotyledonous plants, where the internodes are subject to an increased and the leaves to a diminished growth when the plant is placed in the dark. Similar phenomena are observed in the case of monocotyledons and cryptogams. Methyl alcohol when applied to the roots of plants causes them to die off, and has the same effect as light in promoting the formation of chlorophyll in the cells. Under the influence of methyl alcohol, young plants live longer in the dark, and their weight

when dried is greater than in the case of plants which have not been placed under the same influence. J. K. C.

**Action of Ozone on the Colouring Matters of Plants.** By A. R. LEEDS (*Chem. News*, 40, 86).—In the first trial, in which many varieties of flowers were exposed during nineteen hours to the action of a current of 152 litres of air, containing in all 228 mgrms. of ozone, the bleaching effected was extremely imperfect. When 1,200 litres of air were passed over various flowers (total ozone 1·8 grams), they were partly or wholly bleached at the end of five days. A piece of calico with a pattern in bright green and black was completely bleached during the same interval, the green having disappeared completely, and the stain of the mordant only remaining where the black had been.

From these and other results, it is concluded that the colouring matters of both leaves and flowers of the species (*Lantana*, *Fuchsia*, *Petunia*, *Rosa*, *Verbena*, *Pelargonium*, *Bouvardia*, *Euphorbia*, &c.) experimented with were partly or wholly destroyed by ozone; but a considerable percentage of ozone is required to produce this result, or if such small amounts as are obtained in the customary methods of ozonising air by phosphorus are employed (1 to 3 mgrms. per litre), a large volume of ozonised air must be used, and a considerable interval elapse before bleaching is effected. D. B.

**Distribution and Functions of Asparagine in the Vegetable Kingdom.** By J. BORODIN (*Bied. Centr.*, 1879, 357—360).—Asparagine, according to Pfeffer, occurs only in a few plants, and in these only at the time of germination. The author finds, however, that asparagine is present at the time of budding in most plants, and also when they are in bloom. It appears to be a decomposition-product of albumin, and is formed when there is a lack of carbohydrates in the plant. When these, however, reappear, the asparagine is reconverted by their agency into albumin. From his researches, the author concludes that in the early processes of growth there is a lack of these carbohydrates, and therefore asparagine is formed at these periods, being afterwards converted into albumin. J. K. C.

**Mineral Constituents in Hyacinths.** By A. E. ROSEN and KRELAGE (*Bied. Centr.*, 1879, 360—366).—The hyacinths were planted according to size, at the rate of 42, 90, and 196 plants to the square metre. The results of the examination of their mineral constituents may be seen from the following table.

|               | Mineral constituents in grams in each plant. |                  |                  |
|---------------|--|------------------|------------------|
|               | 196 to sq. metre.                            | 90 to sq. metre. | 42 to sq. metre. |
| Blossoms .... | 0·042  | 0·230            | 0·303            |
| Stem .....    | 0·027  | 0·036            | 0·106            |
| Leaves .....  | 0·082  | 0·245            | 0·632            |
| Bulb .....    | 0·146  | 0·355            | 1·380            |
| Roots .....   | 0·022  | 0·022            | 0·311            |
| Total .....   | 0·319  | 0·888            | 2·732            |

From this table, it is at once evident that the mineral constituents increase very rapidly with the size of the plant, and also that the quantity extracted from the soil is by no means small. From one hectare alone, when planted with 42 hyacinths to the square meter, would be extracted in one season 1,147 kilos. of mineral substance.

The following table shows the difference in quantity of mineral matter in the bulbs when taken out of the ground just after the blossoming period and at the end of summer:—

|   | 196 to sq. metre. | 90 to sq. metre. | 42 to sq. metre. |
|---|-------------------|------------------|------------------|
| Bulbs dug out just after blossoming . . . . . | 0.146             | 0.355            | 1.380            |
| At the end of summer. .                       | 0.557             | 0.987            | 2.314            |
|   |                   |                  | J. K. C.         |

**Experiments with Various Sorts of Beet.** By J. LAMEK and C. PORTELE (*Bied. Centr.*, 1879, 368—370).—The authors bring forward an account of the results obtained by growing various kinds of beet. They find that the “mammoth” variety yielded the largest crop, whilst the “imperial” contained the largest percentage (10.7) of sugar.  
J. K. C.

**Formation of Nitric Acid in the Soil.** By HÜNEFELD, E. REICHARDT, and HERTZ (*Bied. Centr.*, 1879, 327).—According to a former paper of Hünefeld’s, nitric acid is produced when the higher oxides of manganese are brought into contact with air, water, and magnesium carbonate. To confirm this statement, Reichardt and Hertz performed the following experiments. Hydrated oxide of manganese, together with various oxides and earths, such as magnesium and calcium carbonates, alumina, and oxide of iron, were placed with a little water in a large flask, which was then closed and shaken at intervals, care being taken to ascertain that no nitric acid was present at the beginning of the experiments. No nitric or nitrous acid was obtained when the manganese was used in conjunction with calcium carbonate or oxide of iron and alumina, but when mixed with magnesia or alkaline carbonates, nitric acid was recognised in the product. Pyrolusite gave the strongest reactions, and it was found that 50 grams put in a litre flask with 500 c.c. of water after standing for eight days and frequent agitation yielded 0.055 gram of nitric acid.  
J. K. C.

**Calcium Carbonate in Water filtered through Dry Soil.** By F. H. STORER and S. LEWIS (*Bied. Centr.*, 1879, 328—331).—The authors find that a soil which has been ignited at a temperature just sufficient to destroy the organic matter yields calcium carbonate when treated with pure water, even after it has just cooled. They have arrived, therefore, at the conclusion that when ignited at a low temperature, a soil has the power of still retaining carbonic acid. When a dried soil is treated with water containing carbonic acid, part of the latter is retained by the soil. This, according to Storer, is merely a mechanical result, and is due to the adhesion of the gas to the solid particles of the soil.  
J. K. C.

**Mill Waste for Manure.** By FRIEDBURG (*Bied. Centr.*, 1879, 386).—This waste, consisting chiefly of dust and chaff from rye, was found on analysis to contain the following percentages of constituents:—Phosphoric acid, 0·96; nitrogen, 1·80; water, 5·80; organic substance, 62·84; ash, 31·36.  
J. K. C.

**Analyses of Marl.** By J. KÖNIG (*Bied. Centr.*, 1879, 385).—The following are the results of the analysis of 85 samples from Westphalia:—The calcium carbonate varied from 1·36 to 94·83 per cent.; magnesium carbonate was present in 21 samples, and in quantity from 0·38 to 27·39 per cent. Phosphoric acid varying in amount from 0·029 to 1·55 per cent. was found in 23 samples. Lastly potassium was estimated in 28 samples, and varied from 0·08 to 2·43 per cent.  
J. K. C.

**Influence of the Physical Condition of Superphosphate on its Value.** By P. WAGNER (*Bied. Centr.*, 1879, 336—339).—The soluble phosphoric acid in superphosphate on coming into contact with the lime of the soil is converted into an insoluble form, and consequently does not penetrate into the soil; this is especially the case with a soil which contains much limestone, the author finding in one experiment that 93 per cent. of the soluble phosphoric acid had, after three hours' contact with a calcareous soil, become insoluble; the more quickly this conversion takes place, the less is the penetrating power of the phosphoric acid, and the more necessary it becomes to have the superphosphate in as fine a state of division as possible, and well mixed with the soil.  
J. K. C.

**The Shells of Crabs, Oysters, Mussels, &c., as Manure.** By F. H. STORER and J. A. HENSHAW (*Bied. Centr.*, 1879, 331—336).—The authors have made several analyses of the shells of these animals, with a view to ascertain their value as manure. They find that the shells of oysters and mussels are composed almost entirely of carbonate of lime, and contain very little available phosphorus, nitrogen, or potash, with the single exception of the common small mussel (*Mytilus borealis*), 1000 kilos. of which contain 2·8 kilos. of nitrogen. On the other hand the shells of crabs and crawfish are tolerably rich in fertilising materials, the king-crab (*Limulus americanus*) containing as much as 12·5 per cent. of nitrogen, the agricultural value of which being, however, probably less than that of the nitrogen in guano. On the whole, the shells of oysters and mussels may be used with advantage as a lime manure, especially after burning, whereby the small percentages of phosphorus and potash are increased, and in those countries where they are cheaper than calcined limestone.

J. K. C.

## Analytical Chemistry.

**Specific Gravity of Liquids.** By L. SIEBOLD (*Analyst*, 1879, 189).—From experiments carried out by the author, it is clearly shown that hydrometers afford reliable indications of the specific gravity of liquids, no matter whether their gravity is due to substance dissolved or in suspension.  
L. T. O'S.

**Analyses of Organic Compounds containing Fluorine and Boron.** By F. LANDOLPH (*Ber.*, 12, 1586—1588).—In the determination of carbon and hydrogen in such compounds, the author recommends the use of fused lead chromate, which is placed before the copper oxide and only heated gently, as otherwise the boric acid is volatilised. To determine the fluorine and boron, the compound is decomposed by a solution of calcium chloride. The fluorine is thus separated as calcium fluoride, and the boric acid remaining in solution is determined as magnesium borate.  
P. P. B.

**Direct Separation of Manganese from Iron.** By F. BEILSTEIN and L. JAWEIN (*Ber.*, 12, 1528—1531).—The author describes two processes, both of which are preferable to the ordinary method of separating the iron as basic acetate. The first depends on the fact that all the manganese is precipitated as peroxide or sesquioxide from a solution of manganocyanide of potassium, on addition of iodine, whereas no precipitate is produced in potassium ferrocyanide by iodine. The details are as follows: The solution of ferric and manganous salt is poured into excess of concentrated solution of potassium cyanide. A minute insoluble residue always remains, which contains only iron; it is removed by filtration. Iodine is then added until all the cyanide has been decomposed, and the slight excess is removed by addition of a few drops of soda. The precipitated oxide of manganese is filtered off, washed, and dissolved in hydrochloric acid, and estimated as sulphide. The only disadvantage of the process is the large amount of iodine required (about 30 grams), but as it can be nearly all recovered by addition of crude nitric acid to the filtrate from the manganese precipitate, this inconvenience is removed.

The second process depends on the conversion of salts of manganese into peroxide by boiling with strong nitric acid and potassium chlorate. The salts are dissolved in nitric acid, sp. gr. 1.35, and after the solution has been heated to boiling, potassium chlorate is added until all manganese is precipitated. The liquor is then diluted and filtered. The precipitate contains iron, but by dissolving it in hydrochloric acid and repeating the process, it contains only an infinitesimal trace of iron. Both of these processes are applicable to the estimation of manganese in cast-iron and steel.\*  
W. R.

\* The second of these processes has been suggested by Hannay (*this Journal*, 1878, *Trans.*, 269).—W. R.



**Estimation of Organic Nitrogen in Natural Waters.** By H. PELLET (*Compt. rend.*, 89, 523).—The ammonia is estimated by Boussingault's process; the nitric acid, in three litres of water, by Schloesing's method; and the total nitrogen by evaporating three litres of water to dryness, with addition of a small quantity of magnesia, mixing with a small quantity of starch, and heating with soda-lime in the ordinary way. The starch converts the nitric acid into ammonia, if the nitric acid does not exceed 0.25 gram of potassium nitrate. C. W. W.

**Notes on Some Analyses of Waters.** By T. L. PHIPSON (*Chem. News*, 40, 1).—The author considers that a very long experience is necessary for a chemist to decide whether a water is fit for drinking purposes or not; other questions such as its effect in attacking and dissolving lead, or corroding iron pipes or boiler plates have often to be decided by the chemist.

For deciding the questions as to the adaptability of water for drinking purposes, much stress has been laid upon the proportion of organic matter, but this is a mistake, because some waters containing as much as 6 or 8 grains per gallon may be drunk with impunity, whilst others containing much less are known to be exceedingly injurious, if not fatal.

Four or five grains of crenate of ammonia per gallon is not at all hurtful, whilst putrid organic matter, numerous Bacteria and Micrococcus and minute white fungoid growths are sources of imminent danger.

He gives the following as examples of water which he has analysed:—

(1.) *Well near Sleaford (Lincolnshire)*.—Water not quite clear, slightly alkaline with decided saline taste, and well aerated with air and carbonic acid; contains some minute green algæ; total residue, 169 grains per gallon, which is composed of:—

| Organic matter. | NaCl. | Na <sub>2</sub> CO <sub>3</sub> . | Na <sub>2</sub> SO <sub>4</sub> . | K <sub>2</sub> SO <sub>4</sub> . | MgCl <sub>2</sub> . | SiO <sub>2</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaCO <sub>3</sub> . |
|-----------------|-------|-----------------------------------|-----------------------------------|----------------------------------|---------------------|--------------------|----------------------------------|---------------------|
| 2.0             | 76.0  | 44.0                              | 35.0                              | 2.0                              | 1.5                 | 1.0                | 0.5                              | 7.0                 |

Total, 169 grains. There were traces of phosphoric acid and of bromine.

(2.) *St. Anne's Well, Buxton (Derbyshire)*, contains mineral matter 18 grains, organic matter 2.0; total, 20 grains per gallon. The mineral matter is composed chiefly of calcium carbonate and sodium chloride, with a little calcium sulphate and traces of iron, silica, cesium, and strontium, but no lithium or rubidium. The water is beautifully clear and tasteless, and is said to have a constant temperature of 80° to 82° F., sp. gr. at 60° 1.008. The fact that this water cures gout is owing probably to its great purity, and to its being drunk warm and in large quantities.

(3.) *Well on Wimbledon Common (Surrey)*, contains mineral matter 26 grains, organic matter and nitric acid 6 grains; total, 32

grains per gallon. The mineral matter is composed principally of calcium carbonate and sulphate, with a small proportion of alkaline salts. It is well aerated, and contains no phosphoric acid. A single drop of a very dilute solution of potassium permanganate gave a rose tint to 200 c.c. of the water, which persisted for several hours. This is an example of a good well water.

(4.) *Well in the Lower Bagshot Sand, near Esher (Surrey).*—The well is 40 feet deep, and is situated about 40 feet from a small cemetery. The water is beautifully bright, clear, and odourless. It attacks and dissolves lead easily, and shows decided indications of nitrates and much chlorides. It contains nitric acid and organic matter 7.0 grains, sodium chloride 14.0, sulphates, carbonates, &c., 37.8; total, 58.8 grains per gallon. A very deceitful water; certainly impregnated and likely to get worse, sp. gr. 1.0032. A spring much farther from the little cemetery gave nitric acid and organic matter 3 grains, mineral matter 21 grains; total, 24 grains per gallon. This water dissolves lead easily.

(5.) *A Yellow Water (South of England),* supposed to be ferruginous, remains clear even on boiling, but gives off a strong marshy odour. Total residue, 2.1 grains per gallon, consists principally of the ulmates of lime and ammonia, a little carbonate of lime, and traces of chlorides, &c.

(6.) *Well at Midland Bank, Birmingham,* contains mineral matter (after calcination) 58.71 grains; total residue, 81.62 grains per gallon. This water contains a very large amount of nitrates and ammonia. It is a bad water for household use, and it is said to corrode metals.

(7.) *Well in an Artificial Manure Manufactory near Southampton.*—The water contains free sulphuric acid 1500 grains, phosphates, calcium sulphate, alkaline salts, &c., 1820 grains.

(8.) *Well at Albany Barracks, London.*—Organic matter and nitric acid 8 grains, mineral matter 72 grains per gallon. Supposed to have caused an outbreak of typhoid.

(9.) *Well near Huntingdon* contained calcium sulphate 36.89 grains, calcium carbonate 15.37, sodium chloride 16.00, organic matter and nitric acid 5.00, silica, magnesia, oxide of iron, &c., 8.74.

(10.) *Water from a Scullery Pump in Bolton Street, Piccadilly.*—Total residue, 1024 grains per gallon. It contained abundance of phosphates, resembled dilute urine, and was said to have caused sickness and diarrhoea.

(11.) *Wells at Putney, S.W.*—The total residue varies from 38 to 120 grains, and some containing from 38 to 48 grains, of which 7 or 8 grains are composed of organic matter and nitric acid, have been used for many years for drinking purposes without having produced any bad effects. Others that yield 60 grains of total residue, of which 10 grains are composed of organic matter and nitric acid, have been prescribed by the medical authorities. Evidence is quoted from an analysis made by the late Dr. D. Thomson to show that although these waters are highly contaminated, they have not changed in composition for 25 years.

The author generalises as follows :—

(1.) The depth of a well has no influence on the quantity of solid residue which a water contains.

(2.) The purer a water, the more easily does it dissolve lead.

(3.) Boiler deposits from all parts of the world with a few exceptions, consist almost entirely (over 90 per cent.) of calcium carbonate.

(4.) The presence of phosphoric acid is always a *bad indication*.

W. T.

**Rapid Estimation of Pure Sugar in Raw and Refined Commercial Sugars.** By P. CASAMAJOL (*Chem. News*, 40, 74—76; 97—98; 107 and 131).—In Payen's process, two alcoholic solutions saturated with sugar are used, and finally absolute alcohol, to wash out the last traces of the sugar-saturated solutions. The first solution is obtained by taking alcohol of 85 per cent. and adding to this 5 per cent. of strong acetic acid; this mixture is saturated with sugar. This addition of acetic acid was made in order to decompose the sucrates, which were a great nuisance to chemists in former days, but in addition, it seems to make the mixture better able to remove the impurities of gummy sugar. This first of Payen's solutions was the one adopted by Dumas in a process published several years ago, which, however, has never been studied by sugar analysts: the author's process is based on this. Dumas proposed to agitate 100 c.c. of the first Payen solution with 50 grams of sugar, filter, and observe the alcohometric degree corresponding to 15°. For every per cent. of sugar less than 100 the solution is said to indicate 1 per cent. less than 74. For sugars having 87 per cent. or more pure sugar, the results agree very closely with those of the saccharometer, even within 0.1 per cent., but for sugars of lower grade the results obtained are not satisfactory.

As nearly one-half of the raw sugars which occur in commerce stand below 87 per cent., there seemed to be little use in a process which was declared to be inapplicable to sugars of low grade. The author found, however, after trying the process several times, that, although the results obtained were mostly unfavourable, it was impossible to dismiss it entirely; for, upon reflecting upon the results, it was found that many questions arose which required to be solved, and on their solution the author based the hope of modifying this process so as to apply it to the analysis of cane-sugars of all grades.

By employing methyl instead of ethyl alcohol, the author succeeded in obtaining, with an alcohometer, results that agree very closely with those of the optical saccharometer, and that with cane-sugars of all classes from the highest to the lowest. After making a great number of trials, it was found that methyl alcohol of 83.5° of the alcohometer (or 87 per cent.), when saturated with sugar, stands at 77.1°. This solution is the one that has given the most accurate results. It is easily obtained by taking methyl alcohol, standing at 83½° by the alcohometer, and saturating it with sugar by the process which Numa Grav suggested to Payen. Since the solution is liable to alteration from loss of alcohol, it is best to test it before using it. When the degree is lower than required, it may be raised by adding more alcohol. If a certain volume *V* of alcohol and water, whose alcohometric degree is *d* is to be raised to *D*, with strong

alcohol of degree  $\Delta$ , if the volume of the latter to be added is called  $x$ , we shall have  $Vd + x\Delta = (V + x)D$ , whence  $x = \frac{V(D - d)}{\Delta - D}$ . Thus to raise 1000 c.c. of alcohol at 81 to 83.5 with alcohol of 92 per cent. where  $d = 81$ ,  $D = 83.5$ ,  $V = 1000$ , and  $\Delta = 92$ , the volume of alcohol of 92 to be added is,  $x = \frac{1000 \times 2.5}{8.5} = 294.1$  c.c. If the addition of alcohol has been too great, the degree may be diminished by adding water very gradually and stirring up the mixture with an excess of sugar. To ascertain the quantity of water the above formula may be used, but it must be noted that  $\Delta = 0$ , and as both numerator and denominator have become negative quantities, the signs may be changed when  $x = \frac{V(d - D)}{D}$ .

Next in importance is the weight of commercial sugar to be taken for 100 c.c. methyl alcohol solution saturated with sugar. At first an arbitrary quantity may be taken and the result noted, which may be corrected by the following consideration. The lowering of the alcohometric degree depends on the water and the soluble impurities contained in the sugar. If a certain weight of sugar is taken, say 45 grams, the result by the alcohol process may be 91.5 per cent. of sugar. If the same sugar is tested by the optical saccharometer and yields 93 per cent. of sugar, it shows that the alcohol process has given too low a result, and this because the solution was too dense. The first result shows in the sugar  $100 - 91.5 = 8.5$  of impurities and water, whilst it ought to be  $100 - 93 = 7$ . To obtain 93 therefore a weight must be taken equal to  $\frac{45 \times 7}{8.5} = 37.05$  grams.

After trying many experiments with solutions of different strengths, it was found that each solution required a different weight. For the saturated solution of 77.1° of the alcohometer, which is the standard solution employed by the author, the weight is 39.6 grams for 100 c.c. of the solution. Instead of using 100 c.c. the author for a long time used only 50 c.c. To be able to use a cylinder in which this volume would give indications, alcohometers had to be employed of small diameter. For 50 c.c. of standard solution the proper weight is 19.8 grams, i.e., half of the one for 100 c.c. This weight was obtained by calculation. Using this weight with 50 c.c. of standard solution, 15 consecutive tests of raw and refined sugars were made, the results obtained showing that the difference between the percentage of pure sugar by the saccharometer and that by methyl alcohol was very slight, the greatest deviation being 0.7. If the operations are made at temperatures different from 15° C. or 60° F. the corrections can be made by using either of the tables of Gay-Lussac or those for the instrument of Tralles. Another correction for the variation of temperature relative to the volume of standard solution to be taken for a weight of sugar equal to 19.8 grams is given in the table—

| At 15° C.  | 20°. | 25°. | 30°. | 35°. | 40°. |
|------------|------|------|------|------|------|
| 19.8 grams | 19.7 | 19.6 | 19.5 | 19.4 | 19.3 |

The following table contains corresponding corrections for methyl alcohol of various strengths saturated with sugar:—

| Degrees of the<br>alcoholometer<br>before<br>saturation. | Degrees of<br>saturation<br>with sugar. | Degree of the<br>saccharometer<br>(Ventzke). | Grams of sugar<br>in 100 c.c. |
|--|---|--|-------------------------------|
| 92.5   | 91.8                                    | 1.7  | 0.44                          |
| 83.5   | 77.1                                    | 13.2   | 3.43                          |
| 82.7   | 76.5                                    | —  | —                             |
| 81.5   | 75.0                                    | —  | —                             |

*Method of procedure in testing.*—The sugar to be tested should not be weighed until everything is ready. The cylinder is filled with the standard solution to a line indicating 50 c.c., and 19.8 grams of sugar are weighed out. This is transferred to a mortar and the standard solution poured in; the whole is then ground until all lumps and large crystals are broken up. The contents of the mortar are now filtered into the cylinder and washed out with the filtered solution. The filtered solution is then tested with an alcoholometer and a thermometer in succession. To the alcoholometric degree, corrected for temperature, is added the difference between 100 and the alcoholometric degree of the standard solution. This sum represents the percentage of sugar. D. B.

**Behaviour of Various Sugars with Fehling's Solution.** By F. SOXHLET and others (*Bied. Centr.*, 1879, 370).—Soxhlet questions the accuracy of the prevailing opinion, that under all circumstances 5 mols. of copper are reduced in alkaline solution by one of sugar, and states that the quantity of copper reduced varies with the dilution of the Fehling's reagent and the amount of the latter present in excess. In the early part of the titration a large excess is present, as is also the case when the oxide of copper formed is weighed, the liquid still remaining blue. Soxhlet, in common with the rest, finds it the best plan to keep two solutions, one of Rochelle salt and soda, and the other of copper sulphate, a sufficient quantity of each being measured out and mixed before each experiment. When a  $\frac{1}{2}$  per cent. solution of dextrose was used it was found that from undiluted Fehling's solution 5.05 mols. of cuprous oxide, and from diluted only 4.85 mols., are precipitated by 1 mol. of sugar in titration. Similar differences are seen when the gravimetric method is used, 5.5 mols. and 4.85 mols. being reduced according as the Fehling's solution was in large excess or only just so. As the amount of sugar is an unknown quantity, the same conditions cannot be exactly preserved during each experiment, and Soxhlet is therefore of the opinion that an accurate analysis by the gravimetric method is impossible. On the other hand, Märcker, Behrend, and Morgen hold that if certain conditions are maintained throughout, the analysis gives accurate results. They recommend using the same quantity of Fehling's solution and the same volume of liquid in every experiment and calculating the result by means of an empirical table. Their method is as follows:—25 c.c. of each part of the Fehling's solution is mixed with a certain quantity of sugar solu-

tion containing not more than 0.12 gram dextrose, and the whole made up with water to 100 c.c. and heated on a water-bath for 20 minutes. The cuprous oxide is then filtered off, washed with 300 c.c. of hot water, and reduced in hydrogen and weighed.

From the various numbers obtained, the authors have compiled the following table, by means of which the amount of sugar may be calculated:—

| Reduced Cu.<br>mgrms. | Dextrose.<br>mgrms. | Reduced Cu.<br>mgrms. | Dextrose.<br>mgrms. |
|-----------------------|---------------------|-----------------------|---------------------|
| 196                   | 111.1               | 152.5                 | 80                  |
| 194.7                 | 110                 | 144.4                 | 75                  |
| 188.5                 | 105                 | 135.8                 | 70                  |
| 182.0                 | 100                 | 127.0                 | 65                  |
| 175.1                 | 95                  | 117.8                 | 60                  |
| 167.9                 | 90                  | 108.2                 | 55                  |
| 160.4                 | 85                  | 98.3                  | 50                  |

or the amount may be calculated by the formula—

$$a = -19.26 + 2.689b - 0.006764b^2,$$

where  $a$  is the copper and  $b$  the dextrose.

The authors consider that by the use of the above table the process gives very satisfactory results.

Soxhlet has also found that the quantities of cuprous oxide obtained by reduction with milk-sugar vary in the same manner as with dextrose, according to the strength of Fehling's solution employed, from 7.4 to 7.67 mols. of copper to 1 of milk-sugar. Rodewald and Tollens maintain, however, that accurate results are obtainable when certain precautions are taken, the experiments being all carried out under the same conditions of volume, strength, &c.; under the conditions which they employ, 1 mol. of milk-sugar reduces 7.47 mols. of copper sulphate.

J. K. C.

**Estimation of Acetyl by Means of Magnesia.** By H. SCRIF (Ber., 12, 1531—1533).—This process has an advantage over the use of soda, inasmuch as magnesia seldom has a decomposing influence on the products of the reaction. The magnesia is prepared by precipitating the sulphate or chloride with caustic soda, excess being avoided. 5 grams of the paste are boiled with 1 to 1.5 grams of the acetyl-derivative and 80—100 c.c. of water for four to six hours in a flask with inverted condenser. After the reaction is over, the liquid is evaporated to one-third of its volume and filtered. the magnesia is then estimated in the filtrate by the usual process, and from its amount that of the acetyl can be deduced.

W. R.

**Test for Phenylglyoxylic Acid.** By L. CLAISEN (Ber., 12, 1505).—Concentrated sulphuric acid, added to a solution of phenylglyoxylic acid in benzene, gives a deep red coloration, changing to intense blue violet. On addition of water, the colouring matter remains dissolved in the benzene and may be obtained by evaporation. The amides and ethers of this acid, as well as benzoyl cyanide, give the same reaction.

Metanitrophenylglyoxylic acid produces a carmine, and orthōnitrobenzoyl cyanide a bluish-green colour, analogous to that produced by treating isatin with benzene and sulphuric acid. W. R.

**Citrate of Iron and Quinine.** By F. W. FLETCHER (*Analyst*, 1879, 191—193).—The author has applied the following modification of Paul's method for testing quinine to the determination of the quantity and purity of the alkaloid in citrate of iron and quinine.

20 grams of citrate of iron and quinine are dissolved in 50 c.c. of water, and shaken with excess of strong ammonia. The mixture is treated with 25 c.c. of ether, and shaken until the alkaloid is dissolved; the two liquids are separated, and the aqueous solution shaken with ether a second and third time. The ethereal washings are mixed together and evaporated to the consistency of a paste at the ordinary temperature, and finally dried at 120°. It is then weighed; the weight multiplied by 5 gives the percentage of alkaloid present. The alkaloid is converted into basic sulphate by adding the requisite quantity of acid. The weight of alkaloid multiplied by 30.86 gives the number of c.c. of decinormal  $H_2SO_4$  required. The liquid is heated until all the substance is dissolved, the solution allowed to cool spontaneously, and the crystalline mass filtered through calico. The volume of the filtrate is taken, and to it 20 c.c. of ether and excess of ammonia are added, and the mixture well shaken. It is then allowed to stand for six hours, when, at the junction of the two liquids, crystals of cinchonine and quinidine will be found. These are collected on a weighed filter, dried at 120°, and weighed.

The crystalline residue is dried at 100° and weighed, and the weight multiplied by 1.18 gives its value as crystallised sulphate of quinine.

L. T. O'S.

**Iodic Acid as a Test for Morphine.** By J. C. BELL (*Analyst*, 1879, 181).—Iodic acid is shown by the author to be most unsatisfactory as a distinguishing test for morphine. Other organic bodies, such as ipecacuanha and guaiacum, reduce iodic acid with separation of iodine. And, moreover, the statement that the colour is not destroyed by ammonia in the case of morphine is incorrect.

L. T. O'S.

**Nitric Nitrogen in Guano.** By R. R. TATLOCK (*Chem. News*, 39, 268—270).—The author was led by experiments made some years ago to believe that a large proportion, and in some cases nearly the whole of the nitrogen present in guano as nitrates was converted by the soda-lime combustion process into ammonia, and estimated as such, and the extent of this change he has since found to depend on the relative proportion of the organic matter to the nitrates present.

He was surprised to find that it was the practice of chemists of large experience in such analyses to determine the ammonia as if the nitrates present were not decomposed; thus a much larger percentage of that substance would be represented than what really existed.

When nitrates are heated with soda-lime, no ammonia is produced, but when heated with soda-lime in presence of organic matter ammonia is produced, and its quantity depends on the nature and proportion of the organic matter employed. The author experimented with

potassium nitrate in presence of different quantities of starch, sugar, camphor, albumin, and wood charcoal, and the following are some of the results obtained :—

|   |   |
|---|---|
| 20 of starch to 1 of nitrate                  | gave 50·74 per cent. of the nitric nitrogen as ammonia. |
| 3 of camphor to 1 of nitrate                  | gave . . . . . 26·38 per cent.                          |
| 1½ of wood charcoal to 1 of nitrate           | gave.. 11·56    ,,                                      |
| 6 of albumin                    ,,        ,,  | .. 49·94    ,,  |
| 6 of sugar                       ,,        ,, | .. 63·35    ,,  |
| 30 of sugar                      ,,        ,, | .. 97·40    ,,  |

They vary somewhat, however, even with the same proportions of the same organic materials.

The author criticises the various processes for estimating the nitric nitrogen in guanos, and concludes that Crum's (*Proc. Glasgow Phil. Soc.*, 1848, 162) is the best, the nitric acid being determined in the nitrometer as nitric oxide. It sometimes happens, however, that a little free nitrogen is evolved at the same time, by the action of the strong sulphuric acid on nitrogenous organic matters. This can be determined by introducing a warm solution of ferrous sulphate into the nitrometer, which absorbs only the nitric oxide present. The author has not yet arrived at a satisfactory solution of the question.

Tatlock's results (*Chem. News*, 39, 281) are criticised by B. J. Grosjean. He says that he published (*ibid.*, 25, 205) some results on this subject, in which he drew attention to the conversion of nitric nitrogen into ammonia by the soda-lime process, but this fact is stated both in Fresenius's "Quantitative Analysis" and in Churich's "Laboratory Guide." The author described encouraging results for the conversion of all the nitric nitrogen into ammonia by the combustion of nitre with sugar and iron filings. His best results were obtained by mixing the nitre with a caustic alkaline solution in a retort, adding iron filings, and distilling the mixture to a pasty mass, which was allowed to cool, powdered, mixed with soda-lime, and a combustion made to determine the residue of the organic nitrogen.

W. T.

**Perchloric Acid as a Test for Alkaloids.** By G. FRAUDE (*Ber.*, 12, 1558—1560).—Perchloric acid of sp. gr. 1·13—1·14 has no action on quinine, quinine, cinchonine, cinchonidine, morphine, codeine, papaverine, veratrine, caffeine, atropine, nicotine, nor conine. When boiled with brucine, it gives a dark sherry colour, with strychnine a reddish-yellow, and with aspidospermine an intense red. Iodic anhydride and sulphuric acid give with brucine an intense orange-yellow; morphine, deep violet, then orange brown; and curarine, pink. These reactions are suitable as lecture experiments.

W. R.

**Koettstorfer's Process for Butter Analysis.** By G. W. WIGNER (*Analyst*, 1879, 183).—The author points out that for the analysis of samples of genuine butter this process may be used, but in cases of doubt, a complete analysis should be made.

L. T. O'S.



**Coefficients of Expansion of Butter, Lard, Fats, &c.** By G. W. WIGNER (*Analyst*, 1879, 183—185).—By comparing the sp. gr. of butter and lard fat, &c., at different temperatures, the coefficients of expansion have been determined.

Butter fat between 100° and 212° F., has the coefficient 0.0434 per degree F. Between 150° and 190° the coefficient is slightly greater than this number, but remains the same for all other temperatures.

*Lard Fat and Butterine.*—The coefficients of expansion of these two bodies are almost identical, that of lard fat being 0.0420 per degree F.

L. T. O'S.

**Specific Gravities of Fats, Resins, &c.** By H. HAGER (*Pharm. J. Trans.* [3], 10, 287).—The fat is melted, dropped into a flat vessel containing alcohol, in such a manner that the point from which the drops are allowed to fall is not more than three centimeters distant from the surface of the alcohol, and that each drop is allowed to fall on a different spot. The fat globules thus deposited are then removed to a liquid, consisting of either alcohol, water, or glycerol, or mixtures of these, until after careful stirring and reduction or increase of the density, by the addition of one or another of the above liquids, the fat globules are held in equilibrium in any part of the liquid. The sp. gr. of the latter is then determined, and this of course at the same time represents the sp. gr. of the fat. Many of the following sp. gr.'s may be used as criteria for distinguishing the various bodies investigated:—

|   | Sp. gr. at 15—16° C. |
|---|----------------------|
| Butter fat, clarified by settling .....     | 0.938—0.940          |
| "      several months old .....             | 0.936—0.937          |
| Artificial butter .....                     | 0.924—0.930          |
| Hog's lard, fresh .....                     | 0.931—0.932          |
| "      old .....                            | 0.940—0.942          |
| Beef tallow .....                           | 0.925—0.929          |
| Sheep's tallow .....                        | 0.937—0.940          |
| Beef and sheep's tallow, mixed 1 : 1 ....   | 0.936—0.938          |
| Butter of cacao, fresh .....                | 0.950—0.952          |
| "      very old .....                       | 0.945—0.946          |
| Butter and beef tallow, 1 : 1 .....         | 0.938—0.939          |
| Expressed oil of nutmegs .....              | 1.016—1.018          |
| Ditto, extracted with CS <sub>2</sub> ..... | 1.014—1.015          |
| Ditto, crystalline .....                    | 0.965—0.966          |
| Stearic acid, melted, and in drops .....    | 0.964                |
| "      crystalline .....                    | 0.967—0.969          |
| Wax, yellow .....                           | 0.959—0.962          |
| "      African .....                        | 0.960                |
| "      yellow and resin, 1 : 1 .....        | 0.973—0.976          |
| "      "      and paraffin, 1 : 1 .....     | 0.916—0.919          |
| "      "      and yellow ceresin, 2 : 1 ..  | 0.942—0.943          |
| Ceresin, yellow .....                       | 0.925—0.928          |
| Wax, Japan .....                            | 0.977—0.978          |
| "      "      very old .....                | 0.968—0.970          |
| "      white, very old and true .....       | 0.963—0.964          |
| "      "      new .....                     | 0.916—0.925          |

|  | Sp. gr. at 15—16° C. |
|--|----------------------|
| Wax, Japan, new, and stearic acid, 1:1..                                 | 0.945                |
| Wax, sp. gr. 0.963, and stearic acid,<br>sp. gr. 0.963, mixed, 1:1 ..... | 0.975                |
| Ceresin, very white, pure .....  | 0.905—0.908          |
| „ white .....  | 0.923—0.924          |
| Araucaria wax .....  | 0.990                |
| Resin (fir. pine), yellow, transparent ..                                | 1.083—1.084          |
| „ whitish, opaque .....  | 1.044—1.047          |
| Shellac, light-coloured .....  | 1.113—1.114          |
| „ darker .....   | 1.123                |
| Dammar, old .....  | 1.075                |
| Copal, East and West Indian .....  | 1.063—1.800          |
| Benzoin, Siam .....  | 1.235                |
| „ Penang .....   | 1.145—1.155          |
| „ Borneo .....   | 1.165—1.170          |
| Guaiac resin, pure .....   | 1.236—1.237          |
| Amber .....  | 1.074—1.094          |
| Sandarac .....   | 1.038—1.044          |
| Mastic .....   | 1.056—1.060          |
| Balsam of tolu, old brittle .....  | 1.231—1.232          |

## D. B.

**Testing Drugs.** By L. SIEBOLD (*Analyst*, 1879, 190—191).—The method for the detection of mineral adulteration in flour by means of chloroform (C. Himly, *Year Book of Pharmacy*, 1877) may be applied for the same purpose to drugs. The powdered drug is shaken with chloroform when the mineral matter sinks to the bottom, and in the cases of acacia, tragacanth, starches, myrrh, Barbadoes aloes, jalap, saffron, cinchonas, nux vomica, mustard, white pepper, capsicum, and guarana, the drugs float on the top. By pouring the chloroform off, the lower stratum of mineral matter may be collected and weighed.

In some cases, however, such as gamboge, scammony, opium, Socotrine aloes, liquorice root, ginger, colocynth, coussa, ipecacuanha, cinnamon, and cardamoms, a portion of the drug sinks with the mineral matter. The test may, however, be applied qualitatively, since adulteration may be detected by a careful inspection of the sediment.

## L. T. O'S.

**Testing Malt.** By W. SCHULTZE (*Biol. Centr.*, 1879, 375—377).—Malt is usually mashed at from 70° to 75° C.: the author finds, however, that the yield obtained at this temperature is always smaller than when the mashing takes place at 60°, 65°, or 70°. The extract is, however, much more quickly produced at the former temperature, only 20 minutes being required at 70° as against 18.5 hours at 60°. No more extract is obtained after the starch has been converted into maltose and dextrin, and it is therefore unnecessary to continue the mashing longer.

J. K. C.

## Technical Chemistry.

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**Production of Photographs exhibiting Natural Colours.** By W. W. ABNEY (*Chem. News*, 39, 282).—The author suggests that the natural colours in the photographs exhibited by Becquerel last year are produced by the oxidation of the silver compounds employed, and are not due to interference.

He has photographed the solar spectrum on silver plates, and on compounds of silver held *in situ* by collodion, in both of which, the spectrum has imprinted itself approximately in its natural colours. In the former, the image is the brighter, but in the latter the spectrum can be seen both by transmitted and reflected light. The colouring matter seems to be due to a mixture of two different sizes of molecules of the same chemical composition, one of which absorbs at the blue and the other at the red end of the spectrum. The author believes it will be possible to preserve the colours unchanged when exposed to ordinary daylight.

W. T.

**Action of Phenol Vapour on Organic Matter at High Temperatures.** By C. V. THAN (*Annalen*, 198, 273—289).—As the result of a series of experiments on a process for disinfection used in the Hungarian Custom House, it is shown that although exposure to a temperature of 137° for three hours retards the development of organic germs, it is incapable of destroying them. If, however, the germs are subjected to the action of the vapour of phenol at 137°, they are completely destroyed. The articles to be disinfected are placed in a leaden chamber (containing phenol), which is provided with an outer jacket. The apparatus is heated over a fire, and by means of an ingenious arrangement, the pyrometer which registers the temperatures rings an electric bell when the temperature exceeds 137°. By opening dampers in the outer jacket, the temperature can be rapidly cooled down to 137°, when the bell will cease ringing.

Written and printed matter, linen, cotton, quilting, lace, white and coloured silk and woollen materials, raw wool, and plain and lacquered leather, were exposed to this treatment without any deleterious effects, excepting the white wool, which acquired a yellowish tint.

Chamois leather is rendered friable by exposure to phenol vapour.

W. C. W.

**Antiseptic Action of Acids.** By N. SIEBER (*J. pr. Chem.* [2], 19, 433—444).—The presence of so small a proportion as 0.5 per cent. of hydrochloric, sulphuric, phosphoric, acetic, or even of butyric acid is sufficient for antiseptic purposes. Phenol is somewhat less active, whilst lactic and boric acids are much less active, 4 p.c. of boric acid being insufficient to prevent putrefaction.

The experiments were made simultaneously with meat and with the pancreas of the ox, in both cases suspended in water, and without exception decomposition occurred sooner in the case of the pancreas.

There was fungoid growth but no Bacteria, when using 0.5 p.c. sulphuric acid, 1.0 p.c. phosphoric, 2 and even with 4 p.c. lactic acid.

The author discusses the question whether the acidity of the gastric juice is of itself sufficient to maintain the healthy action of the stomach, and he inclines to the affirmative opinion, as he found that 0.25 p.c. of hydrochloric acid, about the normal quantity in the stomach, was sufficient to prevent putrefaction for 24 hours in the tissues of meat and ox-pancreas, and when putrefaction did occur, the solution was no longer acid, but neutral.

As antiseptics, dilute solutions of acid salts would be no doubt as active as the acids, for G. Glaser has lately shown that in this respect aluminic acetate is equal to acetic acid. A. J. C.

**Antiseptic Action of Pyrogallol.** By V. BOUET (*J. pr. Chem.* [2], 19, 445—461).—From a number of experiments it has been found that an aqueous solution containing 1—1½ p.c. of pyrogallol, will preserve meat for a month free from micro-organisms and bad smell, and that a 2—2½ p.c. solution will arrest decomposition in putrefying substances, and prevent alcoholic fermentation of grape-sugar. In this latter respect H. Kolbe and E. v. Meyer state in a note that they have already shown that it is far less active than salicylic acid (*J. pr. Chem.* [2], 12, 151).

It also arrests the movements of *Bacillus subtilis* and the formation of mildew. For many antiseptic purposes, such as wound dressings, pyrogallol, it is suggested, may be substituted with advantage for phenol.

It is a question whether the antiseptic action of pyrogallol is due to its power of absorbing oxygen or to some other property which may be common to all the aromatic phenols. A. J. C.

**Spontaneous Oxidation of Manganous Oxides with reference to the Manganese-recovery Process.** By J. POST (*Ber.*, 12, 1537—1542).—The author's experiments were made on a small scale in ordinary evaporating basins, and relate to the influence of "whipping," addition of soap, and to the use of soda or lime in the recovery of manganese. The only noteworthy result he obtained is, that a slight excess of caustic alkali gives a larger yield of manganic oxide than a slight excess of lime, and that a large excess of alkali, whether lime or soda, has no corresponding influence on the proportion of manganese oxidised. W. R.

**Some Analyses of Iron.** By S. KERN (*Chem. News*, 39, 291).—The author states that in many cases the analysis of iron or steel is not a criterion of the quality of the metal; thus a sample of boiler plate which he analysed and found to contain silicon 0.010 per cent., manganese 0.120, sulphur absent, phosphorus a trace, copper 0.028, was found to be of inferior quality by the mechanical tests. This the author attributes to the rolling of the metal having been badly conducted. W. T.

**Separation of Phosphorus and Iron especially with reference to the Manufacture of Steel.** By T. BLAIR (*Chem. News*, 40, 150—152, and 160—163).—The first part of the paper contains a review of the various processes which have hitherto been proposed with this object, and which are well known. With regard to Krupp's or Marje's process for dephosphorising pig-iron by means of the oxides of iron and manganese, some data are given, from which it is probable, although it has not yet been proved experimentally, that manganese iron will work more favourably still than pig-iron. Another point which has not yet been settled is whether it will be possible by addition of a siliceous pig to fit the refined metal for the Bessemer process, for which, as at present constituted, it is not suitable, since the dephosphorising process also eliminates the silicon.

In discussing the Thomas and Gilchrist process, the author mentions that, although it must be admitted that all the initial difficulties have not been entirely surmounted, it is obvious that the great problem as to the dephosphorisation of iron is solved, and that nothing more is wanting than the rapid and effectual removal of the minor difficulties. Briefly the process consists of the following points:—1. A durable basic lining. 2. The addition of basic materials. 3. Removal of phosphorus by blowing after the carbon has been eliminated. As a set-off against the objections as to the cost of the new process may be considered the utilisation of the large deposits of phosphoretic ores in this and other countries, which may be so much more cheaply worked and delivered to the works than hæmatite ores from distant countries, and the prolongation of the lease of life of inland iron-producing districts in all countries, which have their own coal and ironstone.

D. B.

**Bleaching-Sugar Syrups by Ozone.** By A. R. LEEDS (*Chem. News*, 40, 86).—The first specimen operated on was of syrup, which had undergone but one filtration, and was of a brownish-yellow colour. At the close of the bleaching with ozone, the syrup was of a faint straw colour, and of slightly acid reaction. A second trial was made with a syrup which had been twice filtered, but still retained a strong yellow tint. 20 c.c. of the syrup was introduced into a Geisler absorption apparatus, and a slow current of oxygen, ozonised to the extent of 24 mgrms. ozone per litre, passed through it for several hours. When about 100 mgrms. ozone had been brought into contact with the syrup, it had become almost colourless and almost neutral in reaction.

As determined by Behr, the filtered syrup when it came from the refinery contained, in 100 parts, 50 parts of dry substance and 40 parts of dry sugar. The alteration in the course of bleaching is seen in the following table:—

*Effect of Ozone upon Filtered Syrup.*

| Dry substance contains:—      | Unbleached.    | Bleached.      |
|-------------------------------|----------------|----------------|
| Cane sugar (by polariscope).. | 79.7 per cent. | 80.0 per cent. |
| Inverted sugar .....          | 12.7    "      | 12.7    "      |

D. B.

**Experiments on Creaming.** By W. KIRCHNER and others (*Biol. Centr.*, 1879, 377—381).—As the result of numerous experiments, Kirchner comes to the conclusion that pans made of tin are better than wooden pans for the cream to rise in. The other authors have experimented on the cooling of the milk by various processes before churning, and find that a larger yield of butter is usually obtained when the milk has been cooled by ice. J. K. C.

**Experiments on Churning.** By WINKEL (*Biol. Centr.*, 1879, 382).—The author sums up the results of his investigations as follows:—The more carefully the cream is skimmed off, that is, the less milk it contains, the lower the temperature of churning required, the number and swiftness of the turnings remaining the same; or in other words, so much the more quickly will the butter separate at the same temperature and quickness of churning. J. K. C.

**A New Method of Preparing Methyl-violet.** By H. HASSEY-CAMP (*Deut. Chem. Ges. Ber.*, 12, 1275—1276).—When a mixture of one part of benzenesulphonic chloride and two of dimethylaniline is heated on a water-bath, a blue coloration is produced, which gradually becomes more intense, and after some hours the whole is converted into a viscous dark-coloured mass. The colouring properties of this show it to be methyl-violet. Further, when the product is boiled with water, the presence of an oily liquid was observed, which had the characteristic odour of phenyl sulphide. The reaction, therefore, takes place as follows:—
$$\text{C}_6\text{H}_5\text{SO}_2\text{Cl} + 3\text{C}_6\text{H}_5\text{NMe}_2 = (\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4)_2\text{C} \begin{array}{l} \text{C}_6\text{H}_5 \\ | \\ \text{NMe} \end{array} + \text{HCl} +$$

$2\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{SH}$ . Benzenesulphonic chloride and methyldiphenylamine appear to yield diphenylamine blue. P. P. B.

**Transferring Lightfoot-black from one Fibre to Another.** By J. WOLFF (*Chem. News*, 40, 59).—Lightfoot-black dissolves in a strong aqueous solution of aniline hydrochloride, but incompletely, and with a deep greenish-black coloration. The solution obtained in this way mixes with hot water, producing a black-violet liquid, which dyes cotton, wool, and silk of a grey tint. Even the Lightfoot-black on the fibre dissolves in a strong solution of aniline hydrochloride. Some time ago the author dyed a large quantity of China grass yarn with Lightfoot-black, by soaking the yarn thoroughly in a strong solution of aniline hydrochloride and potassium chloride. A small quantity of that yarn treated lately with a strong solution of aniline hydrochloride produced a dark greenish-black solution, whilst the remaining fibre, after washing and drying, showed a dark greenish-grey colour. The greenish-black solution mixed with water dyed cotton a beautiful bluish-grey, and wool and silk a blackish-grey, showing that this colouring-matter itself has a very great affinity for the fibres, without being produced on the fibre as in the Lightfoot process. The shades thus produced on wool and silk are not bright, proving that the Lightfoot-black process is unable to produce fine black shades at all on these animal fibres. The solutions obtained in the above manner

contain too much acid and comparatively small quantities of colouring-matter, so that it is very difficult to dye a deep black with them.

As far as the author knows, this is the first case of transferring Lightfoot-black from one fibre to another.

If the solution of Lightfoot-black in aniline salt solution is neutralised with caustic soda and boiled until all aniline is driven off, a greyish-black powder remains in a light brown-coloured slightly alkaline liquid. The powder filtered from the liquid and washed on the filter with boiling water, consists of two different colouring matters; the one dissolving with a bright red colour in boiling water acidulated with hydrochloric acid, and dyeing cotton and wool of a dull-red shade, which by washing with clear water turns reddish-brown, and by soaping, clear brown; the other consisting of a dark blue-black powder, insoluble in neutral and acidulated water. This is another proof that Lightfoot-black consists of two colouring matters—one dark blue, the other brown.

D. B.

**Aniline Blacks.** By J. WOLFF (*Chem. News*, 39, 270—273; and 40, 3—6).—The author divides aniline blacks into two series, those which are produced in or on the fibre, and those which are first manufactured and afterwards applied to the fibre by the usual process of dyeing.

The first was invented by J. Lightfoot, of Accrington, in 1866, and are extremely well adapted for *printing* black on vegetable tissues, but all attempts to use this process for dyeing have proved more or less unsatisfactory, owing mainly to the difficulty of evenly distributing the colour, and for silk and wool dyeing this difficulty becomes still greater. The basis of the method usually employed to dye by this process is to soak the yarn or woven fabric in aniline hydrochloride, with or without free aniline, and potassium chlorate, with or without the addition of other, especially metallic compounds, and afterwards to expose the goods to the air in a warm room until they are changed to a dark green colour. They are then passed through a warm bath of soda, which develops the black in a short time, or they are passed through a bath of chrome and hydrochloric acid, which produces a much deeper and finer black, which does not turn green.

The Lightfoot blacks can be divided into (1) those which turn green and (2) those which remain black on exposure to the air. The first are the common and the second the oxidised Lightfoot blacks. The shades of these series of blacks run from blue of different shades of grey, and of brown-black to black-brown. The first link of these series is the blue invented by the late F. Crace-Calvert, and obtained by the action on aniline hydrochloride of a smaller quantity of potassium chlorate than that required for the black with use of ferrous sulphate to moderate the oxidation.

The aniline blacks are mixtures of at least two distinct colouring matters, the one a very deep blue, the other browns of different shades. The less toluidine the aniline contains, the bluer will be the black produced by this process; hence it would appear that the brown colouring matter is derived from the toluidines. Again, from their ability to increase the strength of the oxidation, copper, cerium, vana-

dium, and other metallic compounds, even in very minute quantities, have the property of deepening the dark blue-black to a very fine blue-black. Little is known respecting the chemical constitution of the Lightfoot black; Reinbeck says it is a powerful violet-black base forming with acids green-coloured compounds. Muller gives to the black the formula  $C_{12}H_{14}N_2O_{11}$ , but on account of the large proportions of hydrogen and oxygen the author considers it an improbable one. A more trustworthy elementary analysis by Goppelsroeder leads to the formula  $C_{24}H_{20}N_4$  for the common Lightfoot black, which he interprets as  $= 4(C_6H_5)_3N$ . The chemical constitution of the oxidised black he represents as  $(C_6H_5)_3N \cdot O$ , and of the reduced common black as  $HN(C_6H_5) \cdot N(C_6H_5) \cdot N(C_6H_5) \cdot (C_6H_5)NH$ . With potassium-hydrogen sulphate he produces naphthalene pink from this black, thus,  $5C_{24}H_{20}N_4 + 16HKS O_4 = 8N + 16H_2O + 8SO_2 + 4$  of naphthalene pink,  $C_{30}H_{21}N_3$ .

Another chemist, by treatment of Lightfoot's black with aniline, has obtained a fine aniline pink of the formula  $C_{36}H_{23}N_5$ .

All these formulæ of aniline blacks show that they are the products of powerful oxidation taking place simultaneously with considerable condensation. Another interpretation of these results may be given, supported by the production of naphthalene pink above mentioned, and by the property the black has of forming substitution-products with aniline, such as aniline pink,  $(C_6H_4)_2(NH)_4(C_6H_4)_2$ . The oxidised Lightfoot black  $(C_6H_4 \cdot NH)_2O(C_6H_4 \cdot NH)_2$ . The reduced Lightfoot black,  $H_2N \cdot (C_6H_4)_2(NH)_2(C_6H_4)_2 \cdot NH_2$ .

In the aniline blacks which are manufactured first, and then applied to the cloth or yarn, there are two, known by the commercial names "indulin" and "nigrosin." The latter name was given to a product invented by the author in 1862. He also discovered the first link of the indulin series in 1865, by treating the bases of magenta refuse with aniline and acetic acid. The spirit-soluble indulin thus produced was converted by sulphuric acid into water-soluble indulin, fraudulently called by some firms "nigrosin."

Indulin may be manufactured by several methods.

(1.) From magenta refuse, which is treated with boiling water acidulated with hydrochloric acid, to extract completely the salts of mauvaniline, rosaniline, and chrysaniline, and to leave the violaniline salt undissolved, which is then decomposed with impure caustic soda. 10 parts of the impure violaniline thus left are treated with 6 parts of commercial acetic acid (of the equivalent 120), and 20 parts of "aniline for blue," and heated to between  $140^\circ$  and  $160^\circ$ , as long as ammonia is given off and until the mass dissolves and gives the desired shade, in alcohol acidulated with acetic acid. Caustic soda is then added in sufficient quantity to neutralise the 6 parts of acetic acid, and the liberated aniline is driven off by steam. The indulin base thus obtained may then be separated from the soda acetate solution and dried. To convert it into the water-soluble form, 1 part of the base is introduced slowly into 3 or 4 parts of sulphuric acid of  $66^\circ B.$ , heated to  $100^\circ$ , and kept agitated; the acid solution is then heated at  $120$ — $140^\circ$  for about five hours until a sample when taken out, washed with water, and treated with ammonia at  $60^\circ$  or  $70^\circ$  dissolves quickly and



completely. When the process is finished, the whole is washed with water, filtered, and boiled with sufficient soda solution to dissolve and form a neutral salt with it. The solution is then evaporated, and the residue, which is the water-soluble indulin, is dried at a temperature not exceeding 70°. Ammonia is sometimes used instead of soda.

Another way of preparing indulin is by heating 10 parts of pure aniline with 20 of syrupy arsenic acid at 185° or 190°, until it forms on cooling a dull, yellowish, bronze-coloured, brittle substance, which is composed principally of violanilin. Caustic soda is added to the fused mass, to combine with the arsenious and arsenic acids, the free aniline driven off by steam, and the base after being powdered and dried is converted by aniline and acetic acid into indulin in the manner described.

It may also be prepared by a number of different methods based on the action of suitable oxidising or dehydrogenating agents, such as chlorine, nitric acid and its compounds, on pure aniline or suitable aniline salts at a temperature of 185° to 190°. The author gives equations in explanation of these reactions.

In the most soluble indulin blues, the triphenyl-violaniline predominates in quantity, but in many, the mono- and di-phenyl-violaniline and mauvanilines accompany it. Thus indulin may be principally triphenyl-violaniline hydrochloride.

By treating these bases with sulphuric acid, they are converted into the corresponding conjugated acids, from which salts may be obtained by neutralisation. Thus there may be formed sodium triphenyl-violaniline monosulphonate; and the di-, tri-, and tetra-sulphonates may also be obtained. The monosulphonates are insoluble in water, the disulphonates are sparingly, and the tri- and tetra-sulphonates easily soluble. The alkaline salts of all are easily soluble.

These, together with the phenylated mauvanilines, form the principal constituents of water-soluble indulins; they sometimes, however, contain nigrosin-sulphonic acids and their salts.

Spirit-soluble indulin dyes wool, silk, and cotton of different shades of grey. In dyeing, the acidulated alcoholic solution is added to an acidulated cold bath, the goods to be dyed are immersed, and the whole heated to the boiling point and kept there until the desired shade is obtained.

Spirit-soluble indulin dissolves at 115° in 2 to 3 parts of its weight of glycerine acidulated with 5 per cent. of hydrochloric acid, but dyeing with these products is not satisfactory, owing to the liability of their separating from solution and rendering the dyed shades uneven.

The water-soluble indulins dye fabrics of good light and dark shades of grey, even approaching black, but the blacks are not satisfactory either in colour or "fastness."

The third series of aniline blacks is the one of which nigrosin is a link; they are used for dyeing blacks and greys on wool, silk, and leather. They resist well the action of light and air, and their alcoholic solutions are employed with varnish producing oils and resins for making black varnish.

Nigrosin was first manufactured by heating a mixture of 44 parts

of aniline, 20 of stannous chloride, and 11 of nitrobenzene during four hours at  $190^{\circ}$ , and afterwards at  $220^{\circ}$  or  $230^{\circ}$  for five to eight hours more, until a sample poured into water gives to the latter a pale yellow coloration. At this point, the unaltered aniline in the "melt" was driven off by a current of steam. The "melt" separates from the condensed steam, and when powdered and dried constitutes the nigrosin of commerce. The author soon found that the presence of stannous chloride was unnecessary, and assuming that the nitrobenzene acted simply as an oxidising agent, he made experiments, and found that by the action of arsenic acid on a mixture of aniline and aniline salt, a fine nigrosin could be produced. In trying to make the water-soluble nigrosin from a product produced from aniline containing toluidine, a brown-yellow extract was obtained by boiling with water acidulated with hydrochloric acid, and no nigrosin was dissolved, but when boiled with fresh quantities of acidulated water the brown-yellow substance was ultimately removed, and then the nigrosin became soluble.

In the first stage of the process in the production of nigrosin, violaniline is produced, and at this stage a mixture of violaniline and aniline salts remains. When these are heated at  $220^{\circ}$  or  $230^{\circ}$ , the colour of the melted mass changes gradually from violet-blue to dark blue, and later on to greenish-black, whilst ammonia is formed. Triphenylviolaniline (the base of spirit-soluble indulin) when heated with aniline salts as above described, yields also nigrosin in both the soluble and insoluble form, but without the formation of ammonia.

Pure nigrosin is prepared by heating 22 parts of pure aniline hydrochloride with 10 parts of pure syrupy arsenic acid (containing 70 per cent. of dry acid) for four or five hours at  $190^{\circ}$  in glass or enamelled iron vessels, the liquid being agitated from time to time, and afterwards heated at  $220^{\circ}$  to  $230^{\circ}$  until a sample when drawn off dissolves with a faint yellow colour in boiling water. The unaltered aniline is liberated with soda, and it, in company with diphenylamine, is removed with a current of steam; the remaining nigrosin base is washed with boiling water, then dissolved in boiling water acidulated with excess of hydrochloric acid, and precipitated with soda. The precipitated nigrosin is collected on a filter, washed, and again dissolved in acidulated boiling water, and when cold is precipitated by adding common salt. It is further purified by dissolving it in boiling water, filtering, and allowing it to cool, when the nigrosin separates, the process being repeated several times. Nigrosin has a blue colour if pure aniline is used, but if toluidine is present even in small quantities, the black shades of nigrosin are obtained. The author found the formula for the pure nigrosin base to be  $C_{36}H_{27}N_3$ , and for nigrosin itself,  $C_{36}H_{27}N_3ClH$ , but this is also the formula for triphenylviolaniline, the conversion of the one into the other being brought about by intramolecular change.

By dry distillation, nigrosin yields substances belonging to the derivatives of di- and tri-phenyl-diamine, whilst triphenylviolaniline yields diphenylamine and aniline, and from this the author infers the difference in the molecular constitution of these two bodies.

Pure blue nigrosin dissolves in water, producing a dull blue solu-

tion, becoming brighter and greener on the addition of hydrochloric acid. It possesses a remarkable blood-red fluorescence, and all the blue and black nigrosins have this property more or less, and some so strongly that when so little is dissolved in water that no colour can be seen by transmitted light, the solution has the appearance by reflected light as if particles of bright metallic copper were moving about in it. The nigrosins dye yarns and goods slowly and evenly of blue, or blue-black colours, which when deep enough will stand light, air, and soap well, but not the fulling process.

The following mixtures treated in the manner above described, in which aniline salts and arsenic acid are made to react on each other, produce the different shades of blue and black nigrosins.

60 parts of pure aniline hydrochloride, and 10 parts of pure nitrobenzene, yield a dark blue dyeing nigrosin, whilst the same mixture with 1 part of cuprous or cupric chloride added to it yields a fine blue-black.

60 parts of aniline hydrochloride (prepared from aniline containing 2 per cent. of toluidine) and 10 parts of nitrobenzene (made from benzene containing 2 per cent. of toluene) yields a blue-black dyeing colouring matter, which by addition of certain metallic compounds (such as cupric chloride) is much deepened.

In the manufacture of nigrosins, the careful regulation of the temperature is of great importance, otherwise a considerable quantity of bye-products would be formed.

The nigrosins are slightly soluble in weak boiling alkaline solutions, easily soluble in benzene, petroleum, and certain oils, especially when alkaline, with a bright purple colour, and when acid, with a fine green-blue shade. Oxidising agents convert nigrosins on the fibre into dull and reddish-grey violets, whilst reducing agents render them colourless, forming leuco-nigrosins. Nitric acid, even of 1.5 sp. gr., has very little action on these colouring matters. The author gives formulæ showing the typical relations which he assumes to exist between nigrosin and Lightfoot black.

Nigrosin is specially well adapted for dyeing silk a fine black colour without injuring the gloss of the fibre or increasing its weight more than a few per cent.

W. T.

**Production of the Red Colour in Salting Meat.** By A. HART-DEGEN (*Bied. Centr.*, 1879, 478).—Salt added in large quantities prevents the appearance of the red colour, but if it is applied a little at a time, and the meat is afterwards smoked, a better red is obtained.

J. K. C.

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## General and Physical Chemistry.

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**Emission Spectra of Haloid Mercury Compounds.** By B. O. PEIRCE (*Ann. Phys. Chem.* [2], 6, 597—599).—The emission spectra were obtained by passing the electric current through a Geissler tube containing a small quantity of the salt; when the salt is warmed with a Bunsen burner, the mercury spectrum is seen, and as the heat is increased bands appear which differ according to the salt employed.

The measurements were made with a Steinheim spectroscop, the scale of which corresponded as follows with the lines of the spectrum: Si + 81, Na — 100, Hg $\gamma$  — 102.9 and 103.8, Ba $\alpha$  — 111, Hg $\alpha$  — 114, Sr $\beta$  — 157, Hg $\beta$  — 176, Hg $\delta$  — 188, Hg $\epsilon$  — 207.

When mercuric chloride was used, a band appeared at 108 $\frac{1}{2}$  — 100 $\frac{1}{2}$ . The edge of this band was sharply defined on the less refrangible side; but when the salt was strongly heated, a continuous spectrum was observed, stretching for some distance on the more refrangible side.

Mercurous chloride gives the same band, whence it is argued that mercurous chloride is dissociated.

Mercuric bromide gives a band between 131 and 135; mercuric iodide a band between 168 and 172. It is remarked that the bromide band is exactly half way between that of the chloride and that of the iodide.

F. D. B.

**Smoke of an Electric Lamp.** By B. S. PROCTOR (*Chem. News*, 39, 283).—At the Newcastle-upon-Tyne Chemical Society Mr. J. W. Swan exhibited an electric lamp on the incandescent principle, in which the current had to pass through and heat a cylinder of carbon placed between two platinum conductors; this arrangement was placed in a vacuum in a glass vessel, and as the current was too strong the carbon cylinder broke down.

The author examined the glass which enclosed it, and found the inside covered with a sooty deposit which, under a  $\frac{1}{2}$ -inch microscopic objective, appeared nebulous, with some bright specks of platinum here and there. The platinum supports were also covered with the black deposit, which burned off easily on being heated to dull redness. A piece of the glass was treated with aqua regia, and platinum and iron were found in the solution. It is possible that the platinum particles were scattered about by the disruptive discharge, which followed the breaking down of the carbon cylinder.

W. T.

**Thermochemical Investigation of the Oxides and Acids of Nitrogen.** By J. THOMSEN (*Ber.*, 12, 2062—2065).—In order to calculate the heat of formation of the oxides of nitrogen, the following values were determined by experiment:—

| Reaction.                          | Heat of formation. |
|------------------------------------|--------------------|
| $N_2 + H_4 + O_2 = NH_4NO_2$ ..... | 64950 units        |
| $N_2O_3 + O_2 = N_2O_4$ .....      | 39140 "            |
| $N_2O_4 + Aq$ .....                | 15510 "            |
| $N_2 + O$ .....                    | -18320 "           |

Oxidation of an aqueous solution of  $N_2O_4$ .  $N_2O_4Aq + O = +18320$ . From these data, the following results were obtained, which differ considerably from Berthelot's determinations (*Ann. Phys. Chem.* [5], 6, 178):—

|                        | Berthelot.   | Thomsen.     |
|------------------------|--------------|--------------|
| $N_2 + O$ .....        | —            | -18320 units |
| $N_2 + O_2$ .....      | -86600 units | -72790 "     |
| $N_2 + O_3 + Aq$ ..... | -51800 "     | -36460 "     |
| $N_2 + O_4$ .....      | —            | -33650 "     |
| $N_2 + O_4 + Aq$ ..... | —            | -18140 "     |
| $N_2 + O_6 + Aq$ ..... | -14800 "     | + 180 "      |

The following table shows in columns I and II the heat of formation of the anhydrous nitrates; in I by the direct union of their elements, and in II according to the equation  $M' + O_2 + N_2O_4$ . Column III shows the heat of solution of these salts:—

| Nitrates of                 | I.     | II.    | III    |
|-----------------------------|--------|--------|--------|
| Potassium....               | 104660 | 242960 | -17040 |
| Sodium.....                 | 96430  | 226500 | -10060 |
| Lithium ....                | 96800  | 227240 | + 600  |
| Thallium ....               | 43330  | 120300 | -19940 |
| Silver .....                | 13920  | 61480  | -10880 |
| Barium.....                 | 196100 | 229750 | - 9400 |
| Strontium ...               | 190210 | 223860 | - 4620 |
| Calcium .....               | 173590 | 207240 | + 3950 |
| Lead .....                  | 75860  | 109510 | - 7610 |
| $Sr + O_2 + N_2O_4 + 4H_2O$ |        | 231540 | -12300 |
| $Ca + O_2 + N_2O_4 + 4H_2O$ |        | 218440 | - 7250 |
| $Cd + O_2 + N_2O_4 + 4H_2O$ |        | 124870 | - 5040 |
| $Mg + O_2 + N_2O_4 + 6H_2O$ |        | 214530 | - 4220 |
| $Zn + O_2 + N_2O_4 + 6H_2O$ |        | 142180 | - 5840 |
| $Ni + O_2 + N_2O_4 + 6H_2O$ |        | 124720 | - 7470 |
| $Co + O_2 + N_2O_4 + 6H_2O$ |        | 123330 | - 4060 |
| $Cu + O_2 + N_2O_4 + 6H_2O$ |        | 96950  | -10710 |

W. C. W.

**Thermochemical Research on the Carbonates.** By J. THOMSEN (*Ber.*, 12, 2031—2032).—The heat evolved in the formation of the following anhydrous carbonates by the combination of carbonic oxide, oxygen and the metal, is given in column I; the heat evolved by the combination of carbonic acid with the metallic oxide is shown in column III. For the sake of comparison the heat of formation of the corresponding anhydrous sulphates from metal, oxygen and sulphurous anhydride is given in column II.

| Carbonates and<br>sulphates. | I.     | II.    | III.  |
|------------------------------|--------|--------|-------|
| K <sub>2</sub> .....         | 250940 | 273560 | —     |
| Na <sub>2</sub> .....        | 242490 | 257510 | —     |
| Ba .....                     | 252770 | 266490 | 55580 |
| Sr .....                     | 251020 | 259820 | 53230 |
| Ca .....                     | 240660 | 248970 | 42400 |
| Mn .....                     | 180690 | 178790 | —     |
| Cd .....                     | 151360 | 150210 | —     |
| Pb .....                     | 139690 | 145130 | 22580 |
| Ag <sub>2</sub> .....        | 92770  | 96200  | 20060 |

W. C. W.

**Mutual Relations of Potassium and Sodium Alum in Aqueous Solution.** By F. P. VENABLES (*Chem. News*, 40, 198—199).—Two forms of isomorphism between these two salts may be conceived: the formation of a double alkaline alum,  $\text{KNaSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ : and the isomorphous admixture of the two alums in the various crystals. All attempts to prepare the double alkaline alum failed, the isomorphous displacement always being of the second kind, the potassium salt predominating, owing to its being less soluble in water than the sodium salt. Experiments were also made on the solubility of potassium alum in a solution of sodium alum of different strengths and at different temperatures, the results being that 100 grams water containing—

|                                   |     |      |      |      |      |      |      |      |
|-----------------------------------|-----|------|------|------|------|------|------|------|
| Grams sodium alum                 | 4.8 | 10.0 | 12.1 | 15.4 | 21.1 | 33.7 | 55.6 | 76.7 |
| Will dissolve potas-<br>sium alum | 7.8 | 6.1  | 5.7  | 5.3  | 4.7  | 3.8  | 2.7  | 1.7  |

L. T. O'S.

**Law of Dulong and Petit applied to Perfect Gases.** By H. WILLOTTE (*Compt. rend.*, 89, 540—543).—The product  $AC$  of the molecular weight  $A$  into the specific heat at constant volume  $C$  is very nearly the same for all gases. In order therefore that any two gases may be at the same temperature, it is necessary and sufficient that the mean total energy of any molecule whatever shall have the same value in both gases, that is to say, that  $AB^2 = A'B'^2$ ;  $A$  and  $A'$  being the molecular weights of the gases under consideration, and  $\frac{AB^2}{2}$ ,  $\frac{A'B'^2}{2}$ , the means

of the total energies of the molecules of each gas. Two or more gases are at the same temperature, if, when placed in contact with each other they nevertheless preserve their total respective energies unchanged. It may be shown (1) by making use of the theory of Carnot, or (2) by the homogeneity as far as velocity is concerned of the equations relating to the theory of percussion, that if the rule  $AB^2 = A'B'^2$  holds good for any one temperature, it does so for all other temperatures; the question is how far this can be explained from a purely mechanical point of view. It cannot be due to the mutual collisions of the molecules, for Clausius has shown that inter-molecular shocks exert only a disturbing influence in the theory of gases; the author therefore prefers to explain it by molecular collisions against the atoms of a material ether, a gas of exceedingly low density, having its constituent

particles situated at distances very small in relation to the dimensions of the molecules of ordinary gases; a supposition which serves as a basis for several theories.

If  $A$  represents the weight of any molecule endowed with a rapidity of translation  $b_1$ , the arithmetical mean of the quantities of movement representing the forces of percussion due to the displacement of the molecule  $A$ , can be represented by  $\lambda \Sigma A b_1^2 / t$ , the sum  $\Sigma$  being taken during any moment of which  $dt$  is the element,  $\lambda$  being a constant independent of the nature of the molecule under consideration. The sum of the terms calculated for unity of time is approximately  $\Sigma A b_1^2 / t = A B_1^2$ , where  $B_1^2$  is a quantity equal to the mean of  $b_1^2$ .

If in any vessel there are  $n$  molecules whose mass is equal to  $A$ , and  $n'$  whose mass is equal to  $A'$ , the arithmetical law of the forces of percussion acting in unity of time on the mass of ether in question will be  $\lambda(n A B_1^2 + n' A' B_1'^2)$ . Again, if while  $n + n' = \text{const.}$ , the sum just mentioned does not vary when the composition of the mixture is altered, the systems formed by the forces of percussion will not vary either; and again the sum will remain invariable whatever be the ratio  $\frac{n}{n'}$  if  $A B_1^2 = A' B_1'^2$ .

With a mass of molecules whose centres of gravity are fixed, but of which the various parts are endowed with reciprocal movements, it may be found by similar reasoning that in the case of equilibrium of temperature, the energies corresponding to these movements satisfy the relation  $A B_1^2 = A' B_1'^2$ , whence by addition—

$$A B_1^2 + A B_2^2 = A' B_1'^2 + A' B_2'^2 \text{ or } A B^2 = A' B'^2,$$

$\frac{A B^2}{2}, \frac{A' B'^2}{2}$  representing the total mean energies of the molecules.

It is thus seen why the ratio  $\frac{A B^2}{A B'^2}$  is the same for all gases at any determinate temperatures: further by making use of the principle of homogeneity before mentioned, it may be easily demonstrated that if the ratio  $\frac{A B_1^2}{A B_2^2}$  is the same for all gases at any temperature arbitrarily chosen, it will hold good, or very nearly so, for all other temperatures, the value of the ratio varying very slowly with the temperature. (*Phil.*, 89, 568—570). In determining the conditions of equilibrium of temperature in the case of a solid body surrounded by its own vapour, two principal facts have to be established: (1) the influence of the collisions between the molecules of the solid and those of the gas; (2) the influence of the ether. In the first case, on account of the equality of the masses of these molecules, these collisions, far from having a disturbing effect as in the case of a mixture of two gases, are, on the contrary, sufficient of themselves to maintain an equilibrium, if all the molecules have the same mean energy, that is to say, if the  $B^2$  of the molecules of the solid is the same as the  $B^2$  of the molecules of the gas. ( $B^2$  is a quantity such that  $\frac{A B^2}{2}$  represents the total mean energy of a molecule whose weight is  $A$ .)

As far as the ether is concerned, it is obvious that the molecules of the solid are in the same conditions as the molecules of the gas; if  $B^2$  has the same value in both, the total mean energy being then the same, the conditions of equilibrium are determined. As an illustration, if we consider two volatile solids wholly immersed in their own vapour, the two atmospheres being separated from each other by a piston moving in a horizontal cylinder, when the temperature of the system is in equilibrium, the gases on each side of the piston satisfy the equation  $AB^2 = A'B'^2$ , and this equality holds good equally for the solids A and A', since they have the same  $B^2$  as their respective vapours. But the equality  $AB^2 = A'B'^2$  is affected by the collisions of the molecules of the gases against the walls of the cylinder and piston; this disturbing influence obviously diminishes with the degree of expansion of the gases, so that, at the extreme limit, when a vacuum exists on both sides of the piston, the cause of error will disappear, and, since the piston has then become useless, it may be removed. The law may, therefore, be stated as follows:—Given two simple solid bodies in a vacuum but not in contact, whose atomic weights are represented by  $AA'$ , the actual energy of each of these bodies when their temperature is in equilibrium should be such as to satisfy the equation  $AB^2 = A'B'^2$ . From the preceding it follows that the product of the atomic weight of a body by its *absolute calorific capacity* (Hirn), is constant for all simple bodies. For compound bodies, an analogous law may be deduced. The product  $\frac{AC}{n}$  is the same for every substance; A being

a quantity proportional to the weight of the chemical molecule under consideration; C the absolute calorific capacity of the latter; and  $n$  the number of atoms entering into the composition of the molecule.

J. W.

**Variation in the Composition of the Air.** By P. v. JOLLY (*Ann. Phys. Chem.* [2], 6, 520—544).—The analyses of air which have from time to time been made exhibit slight variations in the percentage of oxygen. These differences might be attributed to unavoidable errors in the observations; it appeared, however, that air collected in the same place at different times had not always the same density, and consequently not the same composition; experiments were therefore undertaken to clear up any uncertainty in the matter.

The composition of the air was determined by two separate methods: firstly, by observing its density; secondly, by eudiometric analysis.

In the first method, the air was weighed in a glass globe holding about a litre, and the amount of oxygen which it contained calculated by means of the equation—

$$xW_o + (1 - x)W_n = W,$$

where  $x$  = vol. of O at  $0^\circ$  and 760 mm. in the unit of volume of air.  $W_o$  = weight of contents of the globe when filled with pure oxygen at  $0^\circ$  and 760 mm.;  $W_n$  = weight of contents of the globe when filled with pure nitrogen at  $0^\circ$  and 760 mm.; and  $W$  = weight of contents of the globe when filled with the air at  $0^\circ$  and 760 mm.

It was necessary in the first place to determine the values of  $W_o$  and  $W_n$ . The oxygen used in these determinations was obtained by the



decomposition of water by electrolysis; the nitrogen by passing air over heated copper gauze, which had previously been reduced by hydrogen. It was found that the copper thus reduced retained a considerable amount of hydrogen, which could only be removed by heating it to a red heat in a vacuum. The weighings were conducted with all possible precautions against error, full details of which are given in the paper.

The mean value of  $W_o$  obtained from seven experiments was 1.442545 gram, the probable error being  $\pm .000013$ , that of  $W_n$  obtained from the same number of observations was 1.269455 gram, the probable error being  $\pm .000024$ . The larger probable error in the case of nitrogen must be attributed to the greater difficulty experienced in obtaining the gas in a pure state.

The samples of air, the composition of which was to be determined, were always collected at the same place, about 2 kilometers from the city of Munich. The following table gives the date of collection, the direction of the wind, and the corresponding value of  $W$ . (The experiments were made in 1875-76) :—

|                |      |          |                |        |          |
|----------------|------|----------|----------------|--------|----------|
| Jan. 3 .....   | S W. | 1.305035 | June 7 .....   | W.     | 1.305046 |
| Jan 25 .....   | N.E  | 1.305754 | June 29. . . . | W.     | 1.305397 |
| Feb. 9 .....   | N.W. | 1.305281 | July 15. . . . | N W.   | 1.305239 |
| Feb. 16 .....  | W.   | 1.305099 | July 22 .....  | N.     | 1.305591 |
| March 7 .....  | N.W. | 1.305157 | Aug. 2 .....   | N.E.   | 1.305296 |
| March 18 ..... | S.   | 1.305014 | Aug 29 .....   | N E.   | 1.305169 |
| May 9 .....    | E.   | 1.305200 | Sept. 11 ..... | W.     | 1.305073 |
| May 18 .....   | E.   | 1.305131 | Sept. 17 ..... | S. (P) | 1.304931 |

The greatest weight, 1.305754, was observed during a north-east wind; the least, 1.304931, during a south wind; in both cases the wind had blown for a considerable time in the same direction. The first value of  $W$  corresponds to 20.965 per cent. of oxygen; the second to 20.477.

Before passing to the second method, and to the experiments made by its means, the weights of a litre of oxygen and of nitrogen respectively were obtained from the values of  $W_o$  and  $W_n$  given above. To do this it was only necessary to find the weight of distilled water at  $4^\circ$  which the glass globe would contain. This weight was found to be 1009.412 grams, the weight of a liter of oxygen in the latitude of Munich ( $48^\circ 6'$ ) and at an altitude of 515 meters above the sea level, is therefore 1.429094 gram: that of a liter of nitrogen in the same locality 1.257614 gram. Reducing these values to the latitude and altitude of Paris, we find that in that city 1 liter of oxygen weighs 1.4293684 gram; 1 liter of nitrogen weighs 1.2578731 gram. The numbers found by Regnault were 1.4293802 and 1.256167 respectively; the differences may be due to the differences in the weights used, or to the impurity of the gases used by Regnault.

The composition of the air was determined eudiometrically by first observing the pressure of a given volume of the air at  $0^\circ$  in the eudiometer, then absorbing the oxygen by means of a red-hot copper spiral,

heated by an electric current, and finally observing the pressure of the remaining nitrogen, occupying the same volume at 0°. Determined in this manner the percentage of oxygen is not liable to an error exceeding 0·02 per cent.

The following table gives the results of experiments thus made:—

| Date.            | Oxygen<br>per cent. | Bar.   | Wind. |
|------------------|---------------------|--------|-------|
| June 13 .....    | 20·53               | 714·03 | W.    |
| „ 18 .....       | 20·95               | 717·7  | N.    |
| „ 24 .....       | 20·73               | 716·8  | N.E.  |
| „ 27 .....       | 20·65               | 718·7  | N.E.  |
| „ 31 .....       | 20·69               | 718·1  | N.E.  |
| July 3 .....     | 20·66               | 716·9  | E.    |
| „ 17 .....       | 20·64               | 713·1  | S.    |
| „ 19 .....       | 20·56               | 713·9  | S.W.  |
| „ 27 .....       | 20·75               | 719·9  | N.E.  |
| October 12 ..... | 20·78               | 715·7  | E.    |
| „ 14 .....       | 20·86               | 720·9  | N.W.  |
| „ 15 .....       | 20·83               | 719·3  | E.    |
| „ 16 .....       | 20·75               | 723·3  | E.    |
| „ 21 .....       | 20·84               | 723·0  | E.    |
| „ 23 .....       | 20·84               | 710·6  | N.W.  |
| „ 27 .....       | 21·01               | 721·5  | N.    |
| „ 31 .....       | 20·85               | 714·2  | W.    |
| November 2 ..... | 20·91               | 724·1  | N.E.  |
| „ 10 .....       | 20·56               | 718·2  | S.E.  |
| „ 13 .....       | 20·67               | 707·0  | W.    |
| „ 20 .....       | 20·65               | 708·9  | N.W.  |

These experiments, which were made in 1877, show that the percentage of oxygen varied from 21·01, when the north wind blew, to 20·53 during the west wind.

The density of the air is therefore not a constant number.

F. D. B.

**Relative Space occupied by Gases.** By G. SCHMIDT (*Ann. Phys. Chem.* [2], 6, 612—615).—If the molecular weight of hydrogen = 2, and the density of the air = 1, the molecular volume of a permanent gas is ordinarily set down as—

$$V = 28·8725,$$

it is contended that this number should be 28·8384, on the supposition that the air contains 20·96 per cent. in volume of oxygen, and a table is given of the densities  $d$  of the various gases and vapours, calculated by means of the formula  $s = \frac{m}{v}$ , where  $m$  = the molecular weight.\*

F. D. B.

\* It is clearly shown in the preceding abstract of the paper by P. v. Jolly, that the density of the air is a variable quantity; the value of  $V$  must therefore also be variable, and the densities of gases cannot be expressed in terms of the density of the air.—F. D. B.

**Absolute Expansion of Liquid and Solid Bodies.** By H. F. WIEBE (*Ber.*, 12, 1761—1764).—The force of cohesion which binds together the molecular groups in liquids and solids, is measured by the expansion which these bodies undergo under the influence of heat. The absolute expansion of an atom, *i.e.*, the coefficient of expansion of the atomic volume, bears a relation to the number of atoms which have combined together to form a liquid or solid group of molecules. Since all bodies have the same cohesion at their boiling and also at their melting points, if the absolute expansion is multiplied by the temperature of these fixed points (calculated from the absolute zero), multiples of the coefficients of expansion, 0.00865, are obtained, as is shown in the following table:—

|          | I.<br>Absolute<br>expansion<br>for 1°. | II.<br>B. p. calcu-<br>lated from<br>absolute zero. | Product of<br>I × II. | Coefficient<br>of expansion. m. |
|----------|--|---|-----------------------|---------------------------------|
| S .....  | 0.008015                               | 772   | 2.17682               | 0.008628 × 600                  |
| Se ..... | 0.001872                               | 975   | 1.82520               | 0.00365 × 500                   |
| Zn ..... | 0.000795                               | 1315  | 1.015425              | 0.003485 × 300                  |
| Cd ..... | 0.001188                               | 1135  | 1.318380              | 0.003371 × 400                  |
|          |  | m. p.   |                       |                                 |
| S .....  | 0.008015                               | 388.6   | 1.171629              | 0.003905 × 300                  |
| Se ..... | 0.001872                               | 492.0   | 0.921024              | 0.003607 × 250                  |
| Zn ..... | 0.000795                               | 687.0   | 0.516165              | 0.003641 × 150                  |
| Cd ..... | 0.001188                               | 590.0   | 0.700920              | 0.003503 × 200                  |

When  $\alpha$  equals the atomic weight,  $\rho$  the density,  $\alpha$  the mean coefficient of expansion between the melting and boiling points,  $T$  the temperature of the boiling or melting point (above the absolute zero), and  $\beta$  the coefficient of expansion in the gaseous state; then  $\frac{\alpha\alpha}{\rho} T = \beta m$ .

In this equation  $m$  bears a relation to the number of atoms in the liquid or solid molecule.

The author has investigated homologous series of organic compounds, and obtained the following results:—

|                      | I.<br>Mean absolute<br>expansion (between<br>b. p. and m. p.) for 1°. | II.<br>B. p. calcu-<br>lated from<br>absolute 0°. | III.<br>Product<br>of I × II. | IV.     |
|----------------------|---|---|-------------------------------|---------|
| Formic acid .....    | 0.01326   | 375.0   | 15.6                          | 5.2 × 3 |
| Acetic acid .....    | 0.06828   | 392.3   | 26.2                          | 5.2 × 5 |
| Butyric acid .....   | 0.10235   | 421.0   | 46.8                          | 5.2 × 9 |
| Methyl alcohol ..... | 0.05000   | 341.3   | 17.06                         | 8.5 × 2 |
| Ethyl alcohol .....  | 0.07143   | 353.3   | 25.26                         | 8.5 × 3 |
| Amyl alcohol .....   | 0.12500   | 406.8   | 50.8                          | 8.5 × 6 |

For the acids, the product of the mean absolute expansion for 1°

by the boiling point is equal to the constant 5.2 multiplied by the number of hydrogen atoms contained in the gaseous molecule, + 1. For the alcohols the constant 8.5 is multiplied by half the number of hydrogen atoms in the molecule. W. C. W.

**Diffusion Experiments with Acid Solutions of Mixtures of Salts.** By F. HINTEREGGER (*Ber.*, 12, 1619—1626).—Experiments with mixtures of sulphuric acid and potassium-hydrogen sulphate, and of the latter and potassium sulphate, which were diffused into water, show that the acid diffuses more quickly than the acid salt, and the latter more quickly than the neutral salt. The same was found to be the case with oxalic acid and potassium and sodium oxalates; after a time, however, this relationship is reversed. Monosodic and disodic phosphates gave a result similar to that exhibited by oxalic acid. At first the monosodic phosphate diffuses more quickly, and after some time the disodic phosphate diffuses more rapidly. Hippuric acid diffuses more slowly than sodium hippurate, which is accounted for by the fact that the latter is more soluble than the former.

P. P. B.

## Inorganic Chemistry.

**Allotropic Modifications of Hydrogen.** By J. THOMSEN (*Ber.*, 12, 2030).—The author points out that Tommasi's statement (*Acad. Milan*), that "the heat of formation of potassium chlorate is 9,760, and that of potassium chloride 104,476 units, and consequently 104,476 - 9,760, i.e., 94,716 heat-units, are absorbed in the conversion of potassium chlorate into chloride, contains no less than three errors. The heat of formation of potassium chlorate is 95,840, and not 9,760, the latter number representing the heat evolved in the conversion of potassium chlorate into chloride in the dry way. Instead of 94,716 heat-units being absorbed in the reduction of the chlorate to the chloride, a liberation of 15,370 heat-units takes place. It is obvious that the theoretical speculations based on these incorrect data are valueless.

W. C. W.

**A New Method for Preparing Hydriodic and Hydrobromic Acids.** By G. BRUYLANTS (*Ber.*, 12, 2059—2062).—Hydriodic acid can be easily prepared by heating a solution of iodine (20 grams) in copaiba oil (60 grams) in a retort connected with an upright condenser. The gas is purified by passing it through a drying tube. When the evolution of gas slackens, fresh iodine is brought into the retort, and the process is continued until about 150 grams of iodine have been used.

In the preparation of hydrobromic acid by this method, the bromine must be slowly dropped into the retort containing the oil, and the gas should be purified by passing through three drying towers.

W. C. W.

**Influence of Volume and Temperature in the Preparation of Ozone. A New Ozoniser.**—By A. R. LEEDS (*Annalen*, 198, 30—42).—A solution of potassium dichromate (not necessarily saturated) mixed with sulphuric acid is placed in a suitable vessel, within which a bell-jar can be placed, and pieces of phosphorus are partly immersed in the liquid. It is better, however, to connect three such jars and draw the air through them by means of an aspirator. For this purpose, the necks of the jars are cemented into brass caps, which are screwed to a bar capable of being raised and lowered as in a galvanic battery; the stoppers are replaced by corks covered with paraffin, through each of which pass three glass tubes, one ending just below the stopper, another just above the liquid, and the third bent into a horizontal ring at the end. The first two tubes are connected so as to allow a current of air to be drawn through the apparatus; the third is for lowering or raising the phosphorus. The pieces of phosphorus are melted in watch-glasses to give them a more convenient shape, and are placed on glass plates in glass cells in the liquid. A flexible tube for conveying the ozone from the generators was made of "cerite" ("kerite-schlauch"), and found to answer very well.

A temperature of 24° gives the best results. The maximum amount of ozone obtained was a little over 2.5 mgrms. per litre of air; but as the generator may be connected with the aspirator and allowed to work for any length of time, the supply is unlimited. G. T. A.

**A Possible Cause of Variation of the Proportion of Oxygen in the Air.** By E. W. MORLEY (*Chem. News*, 40, 184—186, and 199—201).—Loomis has proposed the theory that certain great and sudden depressions in the temperature of the atmosphere are caused by the vertical descent of currents of air from cold elevated regions. If such is the case, then the air at the surface of the earth during such depressions may contain a smaller amount of oxygen than the average. Jolly concludes from his experiments that the air at the equator is poorer in oxygen than that at the polar regions, owing to the amount of oxygen consumed in oxidation being greater than that liberated by reduction. Facts, however, do not confirm these conclusions, no difference in the composition of the atmosphere of the two regions having hitherto been detected.

According to the author's views, based on Loomis' theory, air collected at the centre of an area covered by a descending current would, at a given moment, be a sample fresh from the upper atmosphere; whilst a sample collected on one side of this centre would consist of a mixture of *surface* and *upper* air, but still containing a deficiency of oxygen. Although the author has not yet succeeded in making these experiments, he has, while laying plans for the work, conducted experiments on ordinary air, to ascertain what light can be thrown on the changes in composition of the atmosphere. The apparatus used was constructed on McLeod's modification of Frankland and Ward's apparatus, with important modifications, so as to reduce all causes of error to a minimum.

The samples were collected in the open country, in glass vessels, and preserved over mercury freed from carbonic anhydride, and exploded

with pure hydrogen. Some samples were collected in stoppered and capped bottles, which were inverted, and the caps filled with water.

Analyses of air were made daily from 28th December, 1878, to 6th April, 1879, during which period some very marked and sudden depressions of temperature occurred, which were accompanied by a decrease in the quantity of oxygen. The deficiency, however, as might have been expected, was not proportional to the decrease in temperature (see also p. 85 of this volume).

L. T. O'S.

**Preparation of Perbromic Acid.** By G. WOLFRAY (*Annalen*, 198, 95—98).—Kämmerer (*J. pr. Chem.*, 90, 190) has described a method according to which perbromic acid may be obtained by the action of *dry* bromine on *dry* perchloric acid, the latter being prepared at the time by the decomposition of potassium perchlorate by sulphuric acid. The author has repeated this experiment, and finds that the acid thus obtained, corresponding in all respects with that described by Kämmerer, is nothing more than a mixture of perchloric and sulphuric acids. The apparent absorption of the bromine by the perchloric acid is explained by the fact that perchloric acid, when heated with an excess of sulphuric acid, is decomposed into oxygen and chlorine, and it is this latter which takes up the bromine in the above experiment, forming bromide of chlorine: this is volatilised, together with the excess of bromine, during the subsequent concentration of the liquid.

T. C.

**Researches on Nitrous Acid and Nitrogen Tetroxide.** By G. LUNGE (*Dingl. polyt. J.*, 233, 155—165; comp. this Journal, Abst., 1879, 770)—*Second Part.*—*On the Relations of the Acids of Nitrogen to Sulphuric Acid.*—Our knowledge of this relation is not by any means complete. It is well known that nitrous acid, either in the liquid or gaseous form, or produced nascent from the union of nitrogen dioxide with oxygen, is dissolved by sulphuric acid of about 1·7 sp. gr.; but the behaviour of nitrogen tetroxide towards sulphuric acid is not accurately known. The author has shown that it is dissolved by sulphuric acid, forming nitrosulphuric and nitric acids; but according to Weber and Winkler, nitrogen tetroxide is dissolved as such by sulphuric acid of 66° B., producing a reddish-yellow solution, which, when heated, gives off nitrogen tetroxide with violent ebullition, and leaves a liquid having the properties of nitrosulphuric acid. Winkler stated that 28·072 grams of sulphuric acid at 60° B. absorbed 7·397 grams of nitrogen tetroxide, but that on heating gently, the latter was entirely expelled. Weber describes the effects of nitrogen tetroxide on sulphuric acid of different specific gravities, but only qualitatively: thus, sulphuric acid at a sp. gr. of 1·7 absorbs nitrogen tetroxide without becoming coloured: hence it was assumed that the latter was decomposed; at a sp. gr. of 1·55 the sulphuric acid becomes yellow, and hence it was supposed that the greater part of the nitrogen tetroxide was simply dissolved. Acid of 1·49 sp. gr. takes a greenish-yellow colour; acid of 1·41 sp. gr. takes an intense green colour; acid of 1·31 sp. gr. becomes blue and liberates nitrogen dioxide, which escapes with violent ebullition on gently heating. The green

and blue colours were supposed to be due to the formation of nitrous acid, the nitrogen tetroxide having been decomposed into that substance and, nitrogen dioxide. As these results are very important to vitriol manufacturers, the author studied them more accurately, and, as far as possible, quantitatively. The nitrogen tetroxide, prepared from dry fused lead nitrate, was measured off from a burette, and mixed with pure sulphuric acid, which had been diluted to different strengths with water, and the effects of heat upon these mixtures were also noted.

The following are given as examples of the method employed and of the results obtained by the author in carrying out the experiments:—

100 c.c. sulphuric acid of 1·84 sp. gr., to which was added 2 c.c. = 3 grams liquid nitrogen tetroxide, gave a colourless solution with a very feeble odour, recalling that of ozone. The amount of nitrogen dioxide evolved from 1 c.c. of this solution in the nitrometer was determined, and also the amount required to decolorise 10 c.c. seminormal potassium permanganate solution. From the results, the author calculates that his nitrogen tetroxide contained of pure nitrogen tetroxide 93 per cent., and of nitric acid 7 per cent.; but he argues, as in reality the nitrogen tetroxide does not exist as such in the sulphuric acid, but has undergone a decomposition, one part of the tetroxide having been converted into nitric acid at the expense of the oxygen of the other part, whilst the part which has been robbed of its oxygen remains as nitrous acid in combination with the sulphuric acid; then assuming that this lower oxide takes the oxygen from, and decolorises the potassium permanganate, this would give 46·5 per cent. as nitrous acid, and 53·5 per cent. as nitric acid. The other calculations are made on this supposition, that is, it is first assumed that all the nitrogen tetroxide remains as such, and the deficiency in the theoretical amount of oxygen required is calculated as nitric acid; but if, on the contrary, the amount of oxygen required be less than that found by the permanganate process, then he assumes that no nitric acid is present, but that nitrous acid must have been originally present as an impurity.

(I.) The acid was heated to  $280^{\circ}$ , and kept at that temperature for one hour; any free nitrogen tetroxide, if it were present, must have been thus expelled. When the temperature rose to  $200^{\circ}$ , a little red vapour was evolved, and the liquid acquired a golden-yellow colour; but on cooling, it again became colourless.

On analysis the author calculated that 77·9 per cent. of the nitrogen present existed as  $N_2O_3$ , and 21·1 per cent. as  $HNO_3$ ; there is, consequently, he says, a large amount of the nitric acid driven off and another part changed into nitrous acid.

(II.) On continuing to heat for one hour longer, a farther change took place of the same kind, and 94·5 per cent. of the nitrogen remaining existed as  $N_2O_3$ , in combination with the sulphuric acid forming nitrosulphuric acid; whilst 5·5 per cent. remained as  $HNO_3$ , and 18 per cent. of the nitrogen originally present having been expelled by the heating.

(III.) Another experiment was made by adding pure nitric to pure

sulphuric acid, and analysing the resulting mixture, but no change was found to have taken place.

(IV.) On boiling the mixture for half-an-hour, however, red fumes were given off, and the whole of the nitrogen present was converted into nitrous acid, which was found in combination with the sulphuric acid.

That nitric acid is thus broken up has also been demonstrated in another way by Winkler, who collected the oxygen which was evolved from the decomposition.

The author did not find the same result as Winkler with sulphuric acid of  $66^{\circ}$  B. above mentioned, and he explains this by assuming that Winkler employed so much nitrogen tetroxide that it left a large excess beyond that which could combine with the sulphuric acid as nitrous acid: hence the sudden and violent ebullition and liberation of nitrogen tetroxide on heating the mixture.

2 c.c. nitrogen tetroxide added to sulphuric acid of 1.805 sp. gr. was broken up into practically the same proportions of nitrous and nitric acids as in the first experiment, with acid of 1.84 sp. gr.

Other experiments are described in which sulphuric acid of 1.75 sp. gr. was mixed with nitrogen tetroxide and then heated (*a*), so that the vapour evolved might at once escape, and (*b*) where a long tube was attached to the flask in which the mixture was heated, so that the vapour might condense and flow back again to the acid in the flask. In (*a*) nitrous acid, but no nitric acid was found, whilst in (*b*) nitric acid was present but no nitrous acid; this is explained by the fact that it requires concentrated sulphuric acid to combine with and retain the nitrous acid; and in (*a*) the acid became concentrated by evaporation, whilst in (*b*) it remained of about the same strength, and was unable to retain the nitrous acid.

Again, when the mixture was heated on a water-bath at about  $95^{\circ}$ , no such changes occurred.

As Winkler found, that on heating his mixture of acid of  $60^{\circ}$  B. with nitrogen tetroxide, the latter was evolved, he presumed that it existed as a mechanical mixture with the acid. This the author denies, stating that had Winkler examined the acid after boiling, he would have found that it contained nitric acid, and that the nitrogen tetroxide had really undergone decomposition; and further, that he must have heated it considerably above the temperature of boiling water, otherwise no change would have resulted, and no red fumes would have been liberated.

When the amount of nitrogen tetroxide added is in excess of that required to form nitrosulphuric acid, the author is uncertain from analysis whether it exists in the acid in the form of nitrous acid or of nitrogen tetroxide.

W. T.

**Norwegium.** By T. DAHL (*Ber.*, 12, 1731—1732).—The preparation of this metal from the ore has already been described (this *Journal*, Abs., 1879, 890). It melts at  $234^{\circ}$ , and its atomic weight is 145.952 (RO), or 218.928 ( $R_2O_3$ ). It can be separated from bismuth, which it closely resembles, by the solubility of its oxide in alkalis and alkaline carbonates.

W. C. W.



**Constitution of Antimonic Acid.** By P. CONRAD (*Chem. News*, 40, 197—198).—With a view to decide the constitution of antimonic acid, specimens of it were prepared from the pure metal by seven different methods, and carefully analysed.

The antimony was determined as sulphide, with the usual precautions, whilst the water was determined, first by exposure over sulphuric acid, and then by heating in a slow stream of nitrogen, and collecting the water in a weighed calcium chloride tube. The substance was weighed after heating, and any discrepancy between the loss of weight by the substance and the water expelled, was regarded as due to the reduction of the oxide. The loss of water takes place very gradually.

The acid dried over sulphuric acid at the ordinary temperature has the constitution  $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , whereas the acid dried in a current of dry air at the ordinary temperature is represented by  $\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ . At  $100^\circ$ , this loses 3 mols.  $\text{H}_2\text{O}$ ,  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$  being formed; and between  $100^\circ$  and  $200^\circ$  one more mol.  $\text{H}_2\text{O}$  is expelled, leaving  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . Contrary to the statement of Daubrowa (*Annalen*, 186, 110), the anhydrous pentoxide is not formed at  $275^\circ$ , and even at  $300^\circ$  the product still contains  $\frac{1}{2}$  a mol.  $\text{H}_2\text{O}$ . This is driven off only at a red heat when the oxide begins to decompose.

There seems to be reason to believe in the existence of three antimonic acids, corresponding with three acids of phosphorus—

Orthoantimonic acid,  $\text{H}_3\text{SbO}_4 = 3\text{H}_2\text{O} \cdot \text{Sb}_2\text{O}_5$ .

Pyroantimonic acid (metantimonic acid, Fremy)  $\text{H}_4\text{Sb}_2\text{O}_7 = 2\text{H}_2\text{O} \cdot \text{Sb}_2\text{O}_5$ .

Meta-antimonic acid (antimonic acid, Fremy)  $\text{HSbO}_3 = \text{H}_2\text{O} \cdot \text{Sb}_2\text{O}_5$ .

The gradual formation by heat of the second and third acids from the first is similar to the formation of the corresponding acids of phosphorus.

L. T. O'S.

**Salts of Plumbic Acid.** By O. SEIDEL (*J. pr. Chem.* [2] 20, 200—205).—The author has repeated Fremy's research on plumbic acid (*Ann. Phys. Chem.* [3], 12, 490), partly confirming his results.

*Potassium plumbate*,  $\text{K}_2\text{PbO}_3 + 3\text{H}_2\text{O}$ , crystallises in quadratic pyramids;  $a : c = 1 : 1.2216$ . The crystals are efflorescent and are not isomorphous with potassium stannate. The sodium salt has not been obtained in a state of purity. Potassium plumbate does not produce a precipitate in alkaline solutions of tin and aluminium, but impure plumbates are thrown down on boiling a solution of the potassium salt with lime, baryta, and magnesia.

The precipitate which separates out when an alkaline solution of lead oxide is added to potassium plumbate is the hydrated sesquioxide, and not  $\text{Pb}_2\text{O}_3$ , as stated by Fremy. The precipitate is completely soluble in hydrochloric acid; when treated with nitric or acetic acid, or with a hot solution of potash, lead di-oxide remains undissolved.

W. C. W.

**Volatility of Platinum in Chlorine.** By F. SEELHEIM (*Ber.*, 12, 2066—2068).—When a piece of platinum is heated to redness in a

glass or porcelain tube, through which a current of chlorine is passed, crystals of the metal are deposited on the sides of the tube. A sublimate of platinum is also obtained by exposing a porcelain flask containing platinous chloride to a bright red heat. The author discusses the bearing of these experiments on the abnormal density of chlorine at high temperatures observed by V. and C. Meyer (*Ber.*, **12**, 1426).

W. C. W.

*Note.*—In a recent communication (*Ber.*, **12**, 2202), V. Meyer states that, under the conditions in which his experiments were conducted, platinum does not volatilise. He also points out that Seelheim's explanation cannot account for the abnormal vapour-density of iodine, since in these determinations iodine and not platinum iodide was employed.

W. C. W.

## Mineralogical Chemistry.

**Rock Salt from Saltville.** By B. E. SLOAN (*Chem. News*, **40**, 187).—Some specimens of dark brownish-red rock salt obtained from the salt wells at Saltville, Washington Co., Virginia, gave the following results on analysis:—

|       |       |                                       |                                  |                    |
|-------|-------|---------------------------------------|----------------------------------|--------------------|
| NaCl. | KCl.  | CaSO <sub>4</sub> .2H <sub>2</sub> O. | Fe <sub>2</sub> O <sub>3</sub> . | SiO <sub>2</sub> . |
| 89.21 | trace | 4.86                                  | 0.84                             | 4.53               |

The presence of strontium, barium, or lithium could not be detected.

L. T. O'S.

**Livingstonite.** By F. P. VENABLES (*Chem. News*, **40**, 186—187).—Owing to doubts as to the purity of the samples of this mineral analysed by Bárcena, and consequently as to the accuracy of the formula assigned to it by him, the author has at his request examined purer specimens, and the numbers obtained give the formula HgS.2Sb<sub>2</sub>S<sub>3</sub>, instead of 4Sb<sub>2</sub>S<sub>3</sub> + HgS + FeS<sub>2</sub>. Calcium sulphate was present in considerable quantities, but as it occurs only as a matrix, it may be eliminated from the results of analysis. This is the most strongly acid sulphantimonite yet known.

L. T. O'S.

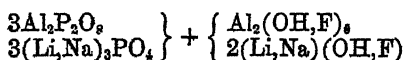
**Magnetite.** By E. C. SMITH (*Chem. News*, **40**, 189).—This mineral occurs in Henry Co., Virginia, in loose crystals coated with ferric oxide, which can easily be washed off, when they present the ordinary black colour and general appearance of magnetic iron ore. Hardness = 6; sp. gr. 4.98. The crystals are strongly magnetic, and are curiously distorted on the surface by step-like projections and depressions, giving them the appearance of rhombic octohedrons, but with irregularly varying inclinations of the general surfaces. The analysis of the cleansed crystals show them to consist of pure magnetite.

L. T. O'S.

**Crystalline Form of Sardinian Anglesite.** By Q. SEITZ (Gazzetta, 9, 344—353).—Anglesite, which is found so frequently and in such fine crystals in the mines of Monteponi and elsewhere in the island of Sardinia, formed the subject of a monograph by Lang, and since then this mineral has been studied by other crystallographers, especially Hessenberg, Zepharowich, and Kreuner. Although the number of forms already described is considerable, a table of no less than 44 being given in the paper, a careful examination of numerous fine crystals has enabled the author to increase it greatly. Details of the measurements of 38 specimens are given, but many of these symbols cannot be considered as definitely established until they have been carefully compared with the results of former workers in this field. In the second part of the memoir the author proposes to discuss the relation between the different forms and the size of the crystals, as well as to give descriptions of other forms of anglesite.

C. E. G.

**Composition of Amblygonite.** By S. L. PENFIELD (*Chem. News*, 40, 208—209).—Brush and Dana (*Am. Jour. Sci.* [3], 16, 42) have shown that triploidite,  $(\text{Mn}, \text{Fe})_3\text{P}_2\text{O}_8 + (\text{Mn}, \text{Fe})(\text{OH})_2$ , is isomorphous with wagnerite,  $\text{Mg}_3\text{P}_2\text{O}_8 + \text{MgF}_2$ , and similar in composition to triplite,  $(\text{Mn}, \text{Fe})_3\text{P}_2\text{O}_8 + (\text{Mn}, \text{Fe})\text{F}_2$ , and consequently argue that the OH-group plays the same part in triploidite as fluorine does in the other two minerals. In amblygonite the author shows that hydroxyl and fluorine are also isomorphous. The results of the analyses give the ratios of  $\text{P} : \text{Al} : (\text{Li}, \text{Na}) : (\text{OH}, \text{F}) = 1 : 1 : 1 : 1$ , corresponding with the formula  $\text{Al}_2\text{P}_2\text{O}_8 + 2(\text{Li}, \text{Na})(\text{OH}, \text{F})$ , or—



Owing to a difference in the optical properties of some specimens, Des Cloizeaux separates the mineral into two varieties, but the variation is so slight as hardly to afford sufficient ground for the distinction.

Details of the method of analysis are given.

L. T. O'S.

**Uranium Minerals from North Carolina.** By F. A. GENTH (*Chem. News*, 40, 210—212).—These minerals, found in the Flat Rock Mine, Mitchell Co., North Carolina, are as follows:—

**Uranotil** occurs as a pale yellow coating on gummite, and is amorphous, massive, and compact. Hardness = 2.5; sp. gr. 3.84; lustre dull. In colour it varies from a straw-yellow to lemon-yellow; its streak is of a pale straw yellow, it is opaque, and has an uneven fracture. The analysis agrees with the formula  $\text{Ca}_2(\text{O}_2)_2\text{Si}_2\text{O}_{18} \cdot 18\text{H}_2\text{O}$ , rather than  $\text{Ca}_3(\text{O}_2)_2\text{Si}_2\text{O}_{18} \cdot 15\text{H}_2\text{O}$  given by Rammelsberg.

**Gummite.**—This orange-coloured mineral occurs in compact, amorphous, nodular masses. Hardness 3; sp. gr. 4.84; lustre resinous; and streak orange-yellow. It is opaque, and has a subconchoidal fracture. It is soluble in acetic acid. Various opinions have been held concerning the constitution of this mineral, and the author, with Patera, maintains that it is principally lead uranate. Gummite is the result of the alteration of uraninite, and that from

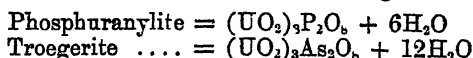
North Carolina is a mechanical mixture, since uranotil penetrates the mass throughout. From the author's analyses it is found to consist of—

|  |                 |
|--|-----------------|
| Uranium hydrate, $H_2(UO_2)O_2 + H_2O$ ....      | 40.10 per cent. |
| Uranotil, $Ca_3(UO_2)_8Si_6O_{21} + 18H_2O$ .... | 33.38 "         |
| Lead uranate, $Pb(UO_2)_2O_3 + 6H_2O$ ....       | 22.66 "         |
| Barium uranate, $Ba(UO_2)_2O_3 + 6H_2O$ ....     | 4.26 "          |

Gummite from Johann Georgenstadt has probably the following composition calculated from Kersten's analyses:—

|  |                |
|--|----------------|
| Uranium hydrate, $H_2(UO_2)O_2 + H_2O$ ....      | 6.32 per cent. |
| Uranotil, $Ca_3(UO_2)_8Si_6O_{21} + 18H_2O$ .... | 30.54 "        |
| Phosphuranylite, $(UO_2)_3P_2O_6 + 6H_2O$ ....   | 8.73 "         |
| Calcium uranate, $Ca_3(UO_2)_8O_3 + 6H_2O$ ..    | 52.99 "        |

*Phosphuranylite* exhibits under the microscope rectangular pearly scales, having a deep brown colour. The analysis shows that it may be expressed by a formula similar to that of *troegerite*.



The analyses of *pittinite* and *eliasite* admit of no calculation, as they appear to contain too many foreign substances. A sample supposed to be *uranite* was found to contain lime and not a trace of copper, and therefore consists of *autunite*. L. T. O'S.

**Analyses of Chrysocolla from Chili.** By N. PELLEGRINI (*Gazzetta*,\* 9, 293).—This specimen of *chrysocolla*, from Cerro Blanco in Chili, was bright green on the outside, farther in it was a beautiful deep green, and in the centre a dark greenish-blue approaching to brown. These were mechanically separated and analysed:—

|                   | Outside. | Second layer. | Centre. |
|-------------------|----------|---------------|---------|
| $H_2O$ .....      | 7.296    | 24.007        | 26.148  |
| $SiO_2$ .....     | 16.621   | 26.685        | 25.938  |
| $CuO$ .....       | 65.306   | 39.891        | 31.913  |
| $Al_2O_3$ } ..... | 4.957    | { 1.499 }     | 9.227   |
| $Fe_2O_3$ }       |          | { †0.415 }    |         |
| $FeO$ .....       | —        | 1.824         | —       |
| $CaO$ .....       | 3.081    | 2.307         | 3.992   |
| Loss .....        | 2.739    | 0.372         | 2.782   |

100.000                  100.000                  100.000  
C. E. G.

**Volcanic Ash from Cotopaxi.** By J. R. SANTOS (*Chem. News*, 40, 186).—This ash, which fell during a recent eruption at Bahia de Caraguez, a distance of 120 miles from Cotopaxi, consisted of a fine brown powder containing glassy granules mixed with ferric oxide. Its specific gravity = 2.743 and its analysis gave—

\* The *Gazzetta chimica italiana* will in future be abbreviated to *Gazzetta*.

† This is perhaps 3.415.—C. E. G.

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | PbO.              | CaO.  | MgO.  |
|--------------------|----------------------------------|----------------------------------|-------------------|-------|-------|
| 56.661             | 19.398                           | 7.523                            | 0.575             | 6.229 | trace |
|                    | Na <sub>2</sub> O.               | K <sub>2</sub> O.                | H <sub>2</sub> O. |       |       |
|                    | 6.123                            | 2.425                            | 0.862             |       |       |

Discarding the iron and water, the above numbers lead to the formula  $(K_2Na_2CaPb)Al_2Si_4O_{14}$ . The quantity of lead contained in this ash is interesting, as is also its state of combination, namely, silicate.  
L. T. O'S.

## Organic Chemistry.

**Tetrabromomethanes.** By R. ANSCHÜTZ (*Ber.*, 12, 2073—2076).—Acetylene tetrabromide, prepared by the direct union of bromine and acetylene, distils without decomposition at 137° under 36 mm. pressure. It is a colourless liquid, which refracts light powerfully, and does not solidify at -24°. It is converted into symmetrical ethylene dibromide (b. p. 110°) by the action of zinc-dust. The dibromide combines with 2 atoms of bromine to form a tetrabromomethane, which is identical with acetylene tetrabromide. Unsymmetrical ethylene dibromide boils at 93°, and readily passes into polymeric modifications. In the latter respect it differs from the symmetrical isomeric.

The tetrabromomethane obtained by Bourgoin (*Ann. Chim. Phys.*, 1873 [4], 29, 378, and 1874 [5], 2, 227) by the action of bromine on dibromosuccinic acid, is considered by the author to be probably ethylene perbromide.  
W. O. W.

**Ferro- and Ferri-cyanides of certain Tertiary Bases.** By C. WURSTER and L. ROSE (*Ber.*, 12, 1822—1827).—The following ferro- and ferri-cyanides are precipitated on the addition of potassium ferro- and ferri-cyanides to a concentrated solution of the corresponding sulphates.

*Nitrosodimethylaniline ferrocyanide*,  $(NMe_2.C_6H_4NO)_2H_4FeCy_6 + H_2O$ , reddish-brown needles, blue by reflected light; *ferri-cyanide*  $(NMe_2.C_6H_4NO)_2H_4FeCy_{12} + 6H_2O$ , silky yellow needles. *Nitrosodimethylmetatoluidine ferrocyanide*, violet-brown needles, containing 5 mols.  $H_2O$ ; the *ferri-cyanide*, yellow needles, containing 4 mols.  $H_2O$ .

*Bromodimethylaniline ferrocyanide*, silver-white plates, containing 2 mols.  $H_2O$ ; the *ferri-cyanide*, yellow crystals, containing 5  $H_2O$ . *Bromodimethylmetatoluidine ferrocyanide*, white crystals with 4  $H_2O$ ; the *ferri-cyanide*, yellow crystals with 9  $H_2O$ .

*Dimethylorthotoluidine ferrocyanide*, white anhydrous needles; *ferri-cyanide*, yellow unstable crystals, containing 9 mols.  $H_2O$ .

*Dimethylmetatoluidine ferrocyanide*, white needles, containing 2  $H_2O$ ; *ferri-cyanide*, yellow needles with 3  $H_2O$ .

*Dimethylparatoluidine ferrocyanide*, white powder, containing 1 mol.  $H_2O$ ; *ferri-cyanide*, yellow needles with 5  $H_2O$ .

*Tetramethylmetaphenylenediamine ferrocyanide*, pearly scales, containing 1 mol.  $\text{H}_2\text{O}$ .

*Tetramethylparaphenylenediamine ferrocyanide*, anhydrous white scales.

The ferricyanides are, as a rule, more soluble than the ferrocyanides.

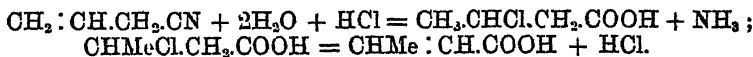
*Nitrosodimethylaniline* is deposited from an ethereal solution in emerald-green triclinic crystals, and from a solution in benzene in dark-green triclinic prisms, containing a molecule of benzene of crystallisation, which is lost on exposure to the air, the crystal losing its transparency. W. C. W.

**Allyl Cyanide and the Products of its Saponification.** By A. PINNER (*Ber.*, 12, 2053—2058).—When a mixture of equal volumes of allyl chloride, alcohol, and water is treated with potassium cyanide for several weeks at the ordinary temperature, potassium chloride separates out, and on distilling the supernatant liquid, *triallylamine* ( $\text{C}_3\text{H}_5)_3\text{N}$  (b. p.  $150^\circ$ ) passes over. The residue in the retort forms two layers; the lighter liquid on fractionation yields propylene cyanide (b. p.  $252\text{--}254^\circ$ ) and ethoxybutyronitril  $\text{CH}_3\text{CH}(\text{OEt})\text{CH}_2\text{CN}$  (b. p.  $173^\circ$ ), described by Rinne (*Ber.*, 6, 389). Pyrotartaric acid is obtained by adding hydrochloric acid to the heavier liquid and extracting with ether.

Potassium cyanide acts very slowly on allyl chloride at the ordinary temperature when alcohol is not present. The sole products of the reaction are allyl cyanide and a small quantity of pyrotartaric acid.

Allyl cyanide dissolves freely in fuming hydrochloric acid: if the solution is left at rest for 12 hours and then neutralised with sodium carbonate, an oily liquid and crystals of crotonamide (m. p.  $159^\circ$ ) are formed. When the hydrochloric acid solution of allyl cyanide is exposed to a temperature of  $50\text{--}60^\circ$  for two hours, ammonium chloride is deposited, and  $\beta$ -monochlorobutyric acid,  $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{COOH}$ , is produced. This acid is very unstable; it boils with evolution of hydrochloric acid at  $200^\circ$ .

The formation of crotonic acid from allyl cyanide may be represented by the following equations:—



An attempt to isolate  $\beta$ -oxybutyric acid by saponifying allyl cyanide with aqueous potash was unsuccessful; crotonic acid was obtained.

On saponification with cold hydrochloric acid, ethoxybutyronitril,  $\text{CHMe}\cdot\text{CH}(\text{EtO})\cdot\text{CH}_2\cdot\text{CN}$ , yields the amide of *ethoxybutyric acid* (m. p.  $71^\circ$ ), and on treatment with warm hydrochloric acid it splits up into ammonium chloride and ethoxybutyric acid (b. p.  $213\text{--}220^\circ$ ). By the action of alcoholic potash on the nitril, a mixture of ethoxy- and hydroxy-butyric acids appears to be formed. W. C. W.

**Action of Bromine on Dichlorhydrin.** By E. GRIMAUD and P. ADAM (*Bull. Soc. Chim.* [2], 32, 18—19).—This paper is devoted to an account of a repetition of Carius' experiments, in which his  
h 2

results are confirmed. By the action of bromine on dichlorhydrin in molecular proportions, a ketone of the formula  $\text{CBr}_2\text{Cl.CO.CH}_2\text{Cl}$  is formed, which on exposure to moist air forms a hydrate containing  $4\text{H}_2\text{O}$ . W. R.

**Mannitol as Bye-product in the formation of Lactic Acid from Cane-sugar.** By DRAGENDORFF (*Arch. Pharm.* [3], 15, 47—49).—3 kilograms of cane-sugar which had been heated for three hours with 15 grams tartaric acid and 13 litres of water, when allowed to stand for 10 days after being mixed with  $1\frac{1}{2}$  kilograms levigated chalk, 120 grams cheese, and 3,600 grams milk, yielded besides lactic acid, 150 grams perfectly pure mannitol, identical with that obtained from manna. Attempts were made on other occasions to obtain a like yield under similar conditions, but they were unsuccessful.

E. W. P.

**Sugar from the Date-palm.** By P. H. DÍON (*Bull. Soc. Chim.* [2], 32, 125—126).—This sugar has the following composition:—

|                                     |       |
|-------------------------------------|-------|
| Saccharose .....                    | 87.97 |
| Glucose .....                       | 1.53  |
| Levulose .....                      | 0.18  |
| Gum .....                           | 4.88  |
| Water and volatile matter .....     | 1.88  |
| Ash .....                           | 0.50  |
| Mannitol, fatty matter, and loss .. | 3.06  |

---

100.00

The sample analysed was undergoing mannitic fermentation, and contained a filiform and a globular ferment, both much smaller than that of beer. The rotatory power of the gum was found to be  $[\alpha]_D = 193.32^\circ$ . A greenish fat was separable from the sugar by treatment with ether. W. R.

**Neutral and Inverted Sugar.** By H. P. DÍON (*Bull. Soc. Chim.* [2], 32, 121—125).—The nature of sugar which does not affect polarised light has not been as yet satisfactorily explained; the author has made it the object of some experiments. When diffused through parchment paper it acquires a laevorotatory power, sensibly equal to that of ordinary inverted sugar, retaining the same reducing action on cupric salts. Now pure sugar, when boiled with alcohol and hydrochloric acid in presence of water just sufficient to hydrate it, becomes inverted, and the solution has no action on polarised light. When this solution is evaporated in a vacuum, the resulting colourless solid is neutral to light when dissolved in water; but when it is evaporated slowly in contact with moist air, a semicrystalline mass consisting of a mixture of glucose and levulose remains, which acts on polarised light like inverted sugar. When ordinary inverted sugar is dissolved in strong alcohol and precipitated with ether, the precipitate, although it reduces Fehling's solution when dissolved in water, has no action on polarised light, but may be converted into the active modification by slow evaporation. The author explains these facts as follows:—Soon

after glucose has been dissolved in water, it has the rotatory power  $[\alpha]_D = +53.23^\circ$ , which slowly decreases after lapse of time. Its alcoholic solution has also  $[\alpha]_D = +53.23^\circ$ , but this does not decrease, whilst the rotatory power of levulose is  $[\alpha]_D = -94.37^\circ$ . When cane-sugar is inverted by boiling with water, a process which demands a lengthened time, its laevorotatory power is zero at first, but gradually increases to  $-21.52^\circ$ . Saccharose is therefore inverted to *neutral sugar*, which if dissolved in alcohol remains neutral, but if brought in contact with water slowly becomes hydrated, and acquires the power of influencing polarised light. In this manner, the author accounts for the neutral sugar noticed by Mitscherlich, as existing in crude sugar and molasses, and which reduces Fehling's solution without affecting polarised light.

W. R.

**Triacetonamine Chromates.** By W. HEINTZ (*Annalen*, 198, 87—90).—When triacetonamine sulphate and potassium dichromate are dissolved in hot water, crystals of dichromate of triacetonamine separate out on cooling, but it may be more readily obtained by mixing 4 parts of chromic acid with 7 parts of crystallised triacetonamine. The crystals are extremely brittle, of a tabular form, and not well formed at the ends. When heated they decompose into triacetonamine, and a brownish-red alkaline liquid, which, when treated with platinum chloride, yields acicular crystals of the triacetonamine platinochloride.

Triacetonamine dichromate is soluble in alcohol, but not in ether. It gives off traces of water at  $100^\circ$ , but is decomposed at a higher temperature, leaving pure chromic oxide. Analysis shows that it consists of  $(C_9H_{15}NO)_2Cr_2O_7$ .

The normal chromate is obtained by mixing solutions of 1 part of chromic acid with 4 parts of crystallised triacetonamine. It crystallises in small yellow prisms readily soluble in water. From a hot solution of this salt orange-red crystals of the dichromate are deposited. The normal chromate exhibits the same deportment as the acid salt when heated, but it dissolves more readily in water. Its formula is  $(C_9H_{15}NO)_4CrO_4$ .

G. T. A.

**Products of Oxidation of Di- and Tri-acetonamine, particularly Amidodimethylacetic, Amidodimethylpropionic, and Imidodimethylaceto-dimethylpropionic Acids.** By W. HEINTZ (*Annalen*, 198, 42—87).—By oxidation with potassium dichromate and sulphuric acid, diacetonamine yields an amidovaleric acid (amidodimethylacetic acid), and an amidobutyric acid (imidodimethylpropionic acid), the amount of the former being relatively greater. Formic and acetic acids are also formed.

When the aqueous solution of the amidovaleric acid is heated with silver oxide, *silver amidodimethylpropionate* is formed, but if silver nitrate is first added to the concentrated aqueous solution of the acid, and then a few drops of ammonia, a crystalline body is obtained which consists of a compound of 2 mols. of silver amidodimethylpropionate with 1 mol. of silver nitrate and 1 mol. of water, which is expelled at  $100^\circ$ . A compound acid can also be obtained by the action of alcohol and hydrochloric acid on amidodimethylpropionic acid, which crystal-



lises in silky needles, and consists of  $C_8H_{12}NO_2Cl$ . A similar body is formed with nitric acid. Platinum tetrachloride combines with the compound of hydrochloric and amidodimethylpropionic acids to form a platinochloride,  $(C_8H_{11}NO_2.HCl)_2PtCl_4$ , which crystallises in the triclinic system.

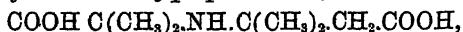
Schneider's amidobutyric acid, obtained from monobutyric acid (*Pogg. Ann.*, 114, 627), is quite different from the amidodimethylacetic acid described above, although the two are isomeric. It is possibly amido-ethylacetic acid.

The amidovaleric acid obtained by Gorup-Besanez from the pancreas, and that prepared by Clark and Fittig from monobromovaleric acid, are also quite different from the author's amidodimethylpropionic acid.

The points of difference between these compounds are given in tabular form in the paper.

The chief product obtained on oxidation of triacetoneamine is imido-dimethylaceto-dimethylpropionic acid, a small quantity of amidodimethylpropionic acid being formed at the same time.

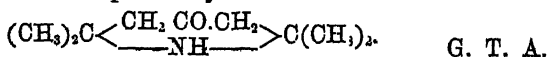
*Imido-dimethylaceto-dimethylpropionic acid,*



forms small colourless crystals which have an acid reaction and a sour taste, and are soluble in hot water, but nearly insoluble in alcohol. The aqueous solution gives no precipitate with lead acetate, mercurous nitrate, picric acid, mercuric chloride, or platinum tetrachloride. The acid volatilises without melting, leaving a small amount of carbonaceous residue. It is anhydrous and dibasic, and forms compounds with acids. A copper, silver, ammonium, barium, and two zinc salts have been prepared. It also forms a double salt with silver nitrate,  $C_8H_{11}AgNO_4 + AgNO_3 + H_2O$ .

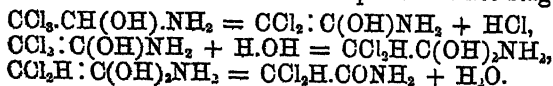
Compounds of the acid with hydrochloric acid, nitric acid, and sulphuric acid have also been prepared, but a platinum double salt does not seem to exist.

From the foregoing experiments the author concludes that the structure of triacetoneamine is expressed by the formula—



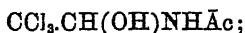
**Action of Potassium Cyanide on Ammoniacal Derivatives of Chloral.** By R. SCHIFF and S. SPECIALE (*Gazzetta*, 9, 335—344).

—When an alcoholic solution of chloralammonia and potassium cyanide is digested for a short time on the water-bath, a violent reaction sets in, and the liquid enters into ebullition, evolving torrents of hydrogen cyanide. On evaporation it leaves a crystalline mass of dichloracetamide,  $CCl_2H.CO.NH_2$ , the yield being so abundant that it is certainly the most convenient method for preparing this substance. The authors consider the reaction to take place in three stages:—



It was thought possible that if compounds of chloral with the sub-

stituted ammonias were treated in the same manner, substances might be obtained which would throw some light on the constitution of acetylchloralammonia, which Schiff considers to be



whilst Pinner contends that its formula should be represented by the formula  $\text{CCl}_3\text{CH}(\text{O}\bar{\text{A}}\text{c})\text{NH}_4$ . The results obtained, however, are complicated, although it seems probable that compounds analogous to dichloracetamide are first found.

Chloral combines directly with dichloracetamide, and the product, when recrystallised from boiling water, forms large lustrous prisms (m. p.  $105^\circ$ ) exceedingly soluble in alcohol or ether. If this substance,  $\text{CCl}_3\text{CH}(\text{OH})\text{NH}\cdot\text{CO}\cdot\text{CCl}_2\text{H}$ , is treated with potassium cyanide in alcoholic solution as above described, it yields nothing but dichloracetamide and potassium dichloracetate.

With chloracetamide, however, prepared directly from chloral and acetamide, potassium cyanide gives potassium chloride and acetate, and a substance which may be extracted by treating the crude product with ether. This forms colourless crystals (m. p.  $120^\circ$ ) which are moderately soluble in ether, alcohol, and hot water, but only very sparingly in cold water. The results of the analysis agree with the formula,  $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_6$ . The authors consider it possible that the compound may be formed as follows:— $2\text{CCl}_3\text{H}\cdot\text{CONH}\bar{\text{A}}\text{c} + 2\text{CCl}_3\text{H}\cdot\text{CONH}_2 + \text{C}_2\text{H}_5\text{O} = 2\text{H}_2\text{O} + 2\text{CCl}_3\text{H}\cdot\text{C}(\text{NH}\bar{\text{A}}\text{c})\cdot\text{N}\cdot\text{CO}\cdot\text{CCl}_2\text{H} + \text{C}_2\text{H}_5\text{O} = \text{C}_{14}\text{H}_{18}\text{N}_4\text{Cl}_2\text{O}_6$ , but notwithstanding this substance gives Lieben's iodoform reaction, indicating the presence of alcohol, the formula given cannot be regarded as definitely established.

Chloralbenzamide,  $\text{CCl}_3\text{CH}(\text{OH})\text{NH}\bar{\text{B}}\text{z}$ , when treated with potassium cyanide in a similar manner, gives rise to a white crystalline substance (m. p.  $131^\circ$ ), very soluble in dilute alcohol. The analyses lead to the formula  $\text{C}_{20}\text{H}_{11}\text{Cl}_2\text{N}_4\text{O}$ , but further investigation is necessary to decide the constitution of this compound.

C. E. G.

**Action of Potassium Carbonate on Isobutaldehyde.** By F. URECH (*Ber.*, 12, 1744—1747).—The thick liquid which the author obtained by treating isobutaldehyde with potassium carbonate (*Ber.*, 12, 193, this Journal, 1879, Abst., 520) is a polymericide of isobutaldehyde, and has the sp. gr. 0.969 at  $24^\circ$ , whilst the sp. gr. of ordinary isobutaldehyde is 0.795 at  $20^\circ$ . On distillation it yields isobutaldehyde and condensation-products which appear to form an acid,  $\text{C}_8\text{H}_{14}\text{O}_2$ , on oxidation.

W. C. W.

**Action of certain Reagents on Parisobutaldehyde.** By F. URECH (*Ber.*, 12, 1747—1749).—Parisobutaldehyde is deposited in crystalline needles, when a mixture of crude isobutaldehyde (containing isobutyl alcohol and acetone) with  $\frac{1}{10}$ th its volume of sulphuric acid, is left at rest for several days. A further yield may be obtained by heating the mother-liquor on a water-bath to expel acetone and unaltered isobutaldehyde, and distilling the residue in a current of steam, when the parisobutaldehyde will crystallise out of the distillate. This compound is also formed when isobutaldehyde is distilled with

small quantities of calcium chloride. Parisobutaldehyde is not attacked by a solution of soda; chromic acid mixture scarcely acts on the body at 100°, but at 130° isobutyric acid is formed. By the action of potassium permanganate at 130°, parisobutaldehyde is converted into acetic acid, and a second acid less soluble in water, which forms crystals melting at 125°.

W. C. W.

**Polymerides of Isobutaldehyde.** By F. URECH (*Ber.*, 12, 1749—1751).—Parisobutaldehyde resembles paracetaldehyde in its properties, and the viscous polymeric modification resembles aldol in many respects, but differs from it in so far that on distillation it not only splits up into water and higher molecular compounds, but at the same time yields isobutaldehyde. The author considers it probable that this substance is a mixture of two polymerides.



I.

II.

W. C. W.

**Preparation of Ethereal Acetates.** By A. P. N. FRANCHIMONT (*Ber.*, 12, 2059).—The acetic derivatives of the carbohydrates and of mannitol are easily prepared by heating the alcohols with four times their weight of acetic anhydride and a small piece of fused zinc chloride.

W. C. W.

**Some Neutral Ammonium Salts: Citrate, Phosphate, and Photosantonate.** By F. SESTINI (*Gazzetta*, 9, 298—304).—These salts were prepared by dissolving the acids in a large excess of concentrated aqueous ammonia, and exposing the solutions over quick-lime under a large bell-jar rendered air-tight by means of mercury. In this way the solution is concentrated in an atmosphere of ammonia, and deposits the neutral salt in crystals which were collected and analysed.

**Triammonium Citrate.**—The crystals are deliquescent, and have an ammoniacal odour, decomposing on exposure to the air. When heated, they rapidly lose water and ammonia, and leave triammonium citrate. Their composition is represented by the formula  $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_4\cdot\text{H}_2\text{O}$ .

**Triammonium Phosphate,**  $\text{PO}_4(\text{NH}_4)_3\cdot 5\text{H}_2\text{O}$ .—The crystals were not sharp enough for goniometric observation. They evolve ammonia on exposure to the air.

**Diammonium Photosantonate,**  $\text{C}_{10}\text{H}_{18}\text{O}_4(\text{NH}_4)_2\cdot 7\text{H}_2\text{O}$ , is deposited in crystalline crusts on evaporating a solution of the acid in excess of ammonia as above described. Like the salts previously mentioned, it has an odour of ammonia.

C. E. G.

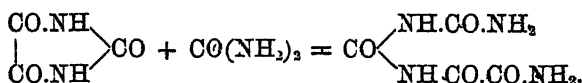
**Urea Platino-chloride.** By W. HEINTZ (*Annalen*, 198, 91—94). When concentrated solutions of urea and platinum tetrachloride are mixed in such proportions that one atom of platinum is present for each two molecules of urea, and the solution is concentrated in a vacuum over sulphuric acid, a crystalline crust is formed on the surface of the liquid. If this crust is constantly disturbed so as to expose fresh sur-

faces of the liquid, the crystals settle down to the bottom of the vessel. They are of a yellow colour, and often have the appearance of rectangular plates, although they are really rhombic prisms.

They are extremely deliquescent, and effloresce in dry air. They are soluble in alcohol but not in ether. They contain two molecules of water, and have the formula,  $(\text{CH}_4\text{N}_2\text{O}.\text{HCl})_2 + \text{PtCl}_4 + 2\text{H}_2\text{O}$ .

When heated, they do not change colour, but evolve much water and carbonic anhydride, whilst ammonium platinochloride is formed, probably together with cyanic and cyanuric acids, and possibly a platinum compound of guanidine. G. T. A.

**New Derivative of the Parabanic Series.** By E. GRIMAUD (*Bull. Soc. Chim.* [2], 32, 120—122).—When an intimate mixture of urea and oxalylurea (parabanic acid) is heated at  $125\text{--}130^\circ$ , the following reaction takes place; the amide of oxalyl-biuretic acid being formed—



The new body is very sparingly soluble in water, and is destroyed by prolonged ebullition. It dissolves in strong sulphuric acid, and is precipitated by water as a jelly.

It gives a violet-pink colour with copper sulphate. When boiled with ammonia, it yields oxalate and urea, along with a trace of biuret. W. R.

**Crystalline Form of some Aromatic Compounds.** By R. PANEGLIANO (*Gazzetta*, 9, 354—364).—*Tribromobenzene* [ $\text{Br}:\text{Br}:\text{NO}_2:\text{Br} = 1:3:4:5$ ].—Monoclinic system,  $a:b:c = 0.651845:1:0.369545$ ;  $\eta = +X: +Z = 99.46^\circ$ . Forms observed, (010), (001), (110), (011), (101), (121). Cleavage parallel to (101), perfect. Twin planes parallel to (101). The angle of the optical axes for ordinary light in oil is about  $60^\circ$ ; ( $\rho < \nu$ ) for the red. The crystals are sensibly dichroic.

*Tribromonitrobenzene* (m. p.  $135.5^\circ$ ).—The crystals are sulphur yellow, and belong to the triclinic system,  $a:b:c = 0.45560:1:0.45717$ . Forms observed, (010), (001), (110), ( $\bar{1}10$ ), ( $\bar{1}11$ ), ( $\bar{1}\bar{1}1$ ), (041). Cleavage parallel to (001) perfect. The angle of the optical axes in oil is about  $74^\circ$ . Dichroism is very distinct on the face (010), the tints being deep lemon-yellow, and almost colourless. The dichroism on (110) and ( $\bar{1}\bar{1}0$ ) is sensibly the same.

*Bromacetanilide*,  $\text{C}_6\text{H}_4\text{Br.NHAc}$ .—Colourless crystals belonging to the monoclinic system,  $a:b:c = 1.53838:1:1.43539$ ;  $\eta = +X: +Z = 117.12^\circ$ . Observed forms, (100), (010), (001), (110), (210), (101), ( $\bar{1}02$ ), ( $\bar{1}01$ ), (012). Cleavage parallel to (101) perfect, but interrupted parallel to (100). There is a plane of maximum extinction, making an angle of about  $52^\circ$  with the plane of symmetry (ordinary light).

*Nitrotoluidine* [ $\text{CH}_3:\text{NO}_2:\text{NH}_2 = 1:2:4$ ].—Monoclinic system  $a:b:c = 1.35781:1:1.75472$ ;  $\eta = +X: +Z = 125^\circ 10'$ . Observed

forms, (110), (001), (011), ( $\bar{1}12$ ), ( $\bar{7}72$ ). Cleavage perfect parallel to (001); laminæ flexible. Twin plane observed parallel to (001). The plane of the optical axes is parallel to the plane of symmetry, and the angle of the axes in oil is about  $77^\circ$  for red light. Dichroism is only sensible in thin laminæ or in very small crystals.

*Nitroiodobenzene*.—The crystals are colourless and belong to the monoclinic system,  $a:b:c = 2.2961:1:1.1297$ ;  $\eta = +X: +Z = 104^\circ 28'$ . Observed combination, (100), (001), (110), (101). Cleavage perfect parallel to (100). Twin plane observed parallel to (100).

*Potassium nitrophenolsulphate*  $[\text{OH}:\text{KSO}_3:\text{NO}_2 = 1:2:4]$ .—The crystals examined were beautifully perfect, and of a straw-yellow colour. They belong to the monoclinic system,  $a:b:c = 1.70451:1:1.52466$ ;  $\eta = +X: +Z = 117^\circ 58' 45''$ . Combinations observed, (100), (110), (101), ( $\bar{1}01$ ), ( $\bar{1}11$ ). The cleavage parallel to ( $\bar{1}01$ ) is perfect. The plane of the optical axes makes an angle of about  $4'$  with the axis  $c$  with ordinary light. Rotatory dispersion ( $\rho < \nu$ ).  $2H_\alpha = 66' 10'$  for red light. The dichroism is distinct, normal to the faces of the vertical prism and of the pinacoid 100: the tints are bright yellow and almost colourless.

*Methylumbelliferic acid*,  $\text{C}_6\text{H}_3(\text{OH})(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .—The crystals belong to the monoclinic system,  $a:b:c = 1.7183:1:3.5017$ ;  $\eta = +X: +Z = 93^\circ 58'$ . Forms observed, (100), (001), (010), (110), (115), ( $\bar{1}15$ ), (015). There is a perfect cleavage parallel to ( $\bar{5}07$ ). The plane of the optical axes is normal to the plane of symmetry. In a lamina obtained by cleavage, the angle of the optical axes in air was  $106^\circ 20'$  for red, and  $107^\circ$  for violet light ( $\rho < \nu$ ).

An account of the two 1:4 acetoluides has already been published in this Journal (Abst., 1879, 626). C. E. G.

**Action of Nitric Acid on Tribromobenzene.** By C. WURSTER and A. BFRAN (*Der.*, 12, 1821—1822).—When tribromobenzene is treated with nitric acid (sp. gr. 1.534) at  $100^\circ$ , mononitrotribromobenzene (m. p.  $142.5^\circ$ ) is formed, and on nitrating this substance with a mixture of nitric and sulphuric acids, dinitrotribromobenzene is obtained in glistening needles (m. p.  $192^\circ$ ). Attempts to prepare trinitrotribromobenzene by this method were unsuccessful.

These results are in direct contradiction to those of Körner (*Gazzetta*, 1874, 422), who states that when nitric acid acts on tribromobenzene no mononitro-derivative is produced, but that a mixture of di- and tri-nitrotribromobenzenes is obtained. W. C. W.

**Cymene from Cumic Alcohol.** By E. PATERNO and P. SPICA (*Gazzetta*, 9, 397—400).—The synthesis of paramethylcumene or isocymene recently effected by Jacobsen (*Ber.*, 12, 429), and the marked difference in properties between it and the known cymene, has confirmed the authors in their opinion that the cumic compounds contain isopropyl, whilst cymene contains normal propyl, and has also removed all doubt as to the identity of the cymene obtained from camphor, from essence of cumin, and from cymyl alcohol by the action of zinc chloride, although in the last-named reaction there must have been a transformation of the isopropyl group into normal propyl. In order further

to elucidate this question, the authors endeavoured to convert cumic alcohol into the paraisopropylmethylbenzene or isocymene of Jacobsen by a different method of treatment. For this purpose, pure cumic alcohol was transformed into *cumyl chloride*,  $C_6H_4(C_3H_7).CH_2Cl$ , by saturating it with dry hydrochloric acid gas, separating the oily layer from the aqueous solution of hydrochloric acid, drying it, and rectifying. The pure chloride was thus obtained as a colourless liquid (b. p.  $230^\circ$ ), which yielded cumic acid and a little terephthalic acid on oxidation, showing that the isopropyl group had not undergone molecular change.

In order to convert the chloride,  $C_6H_4(C_3H_7).CH_2Cl$ , into isocymene,  $C_6H_4(C_3H_7).CH_3$ , it was dissolved in alcohol and treated with hydrochloric acid and zinc. The product submitted to fractional distillation yielded a hydrocarbon boiling at  $175\text{--}178^\circ$ , which when converted into the sulphonic acid gave a barium salt having all the properties of that prepared from ordinary cymene. The sulphonamide also, prepared from the cymenesulphonic chloride, melted at  $114\text{--}115^\circ$ , the melting point of cymenesulphonamide, whilst the corresponding derivative of isocymene melts at  $97\text{--}98^\circ$ . It is evident, therefore, that in the reduction of the chloride, not only is the chlorine in the  $CH_2Cl$  group displaced by chlorine, but at the same time the isopropyl group  $CH(CH_3)_2$  is converted into normal propyl,  $CH_2CH_2CH_3$ .

C. E. G.

**Diamylbenzene.** By A. AUSTIN (*Bull. Soc. Chim.* [2], **32**, 12—13). This hydrocarbon was prepared by heating 750 c.c. of benzene with 50 grams of anhydrous aluminium chloride for some days at  $85^\circ$ , gradually adding 250 c.c. of optically active amyl alcohol.

The product of this reaction, consisting chiefly of amylbenzene, was mixed with a tenth of its weight of aluminium chloride, and boiled with an equal volume of amyl chloride. The product boiled between  $260^\circ$  and  $270^\circ$ , and on analysis gave numbers corresponding with the formula  $C_6H_4(C_5H_{11})_2$ . It is a colourless aromatic liquid, with a taste resembling that of turpentine. It is very mobile. It does not solidify at  $-20^\circ$ . Its sp. gr. at  $0^\circ$  is 0.8668. Its vapour-density was found equal to 8.09: theory, 7.55. It probably belongs to the *meta* series.

W. R.

**Bromodimethylaniline.** By C. WURSTER and A. SCHEIBE (*Ber.*, **12**, 1816—1819).—According to the authors, the monobromodimethylaniline (m. p.  $55^\circ$ ) which Weber (*Ber.*, **10**, 764) obtained by the action of bromine on a solution of dimethylaniline in acetic acid, is not a *meta* but a *para* compound, since on treatment with sodium nitrite it does not yield a nitroso-derivative, but paranitrodimethylaniline (m. p.  $161^\circ$ ) and monobromomonomethylaniline nitrosamine. The latter substance crystallises in white needles (m. p.  $74^\circ$ ), and is reduced by tin and hydrochloric acid to monobromomethylaniline. This base boils at  $260^\circ$ , and decomposes at a higher temperature, forming a substance which dissolves in alcohol, with intense red coloration, and which appears to be dimethylrosaniline.

**Metabromodimethylaniline.**—By the action of methyl iodide and soda on metabromaniline, the compound of this base with methyl

iodide is obtained in crystalline scales (m. p. 201). On distillation in a vacuum, it splits up into methyl iodide and metabromodimethylaniline (m. p. 11°, b. p. 259°). This compound appears to yield a nitroso-derivative (m. p. 148°), and is totally different from Weber's monobromodimethylaniline.

W. C. W.

**Parabromodimethylaniline.** By C. WURSTER and A. BERAN (*Ber.*, 12, 1820).—By the action of methyl iodide and a solution of soda on pure parabromaniline, a compound of methyl iodide and parabromodimethylaniline is obtained in white crystals, which melt with decomposition at 185°. By treating this substance with oxide of silver, parabromodimethylaniline (m. p. 55°) is formed. It is identical in every respect with Weber's (*Ber.*, 10, 763) so-called metabromodimethylaniline.

W. C. W.

**Action of Sulphonic Chlorides on Amines.** By W. MICHLER and K. MEYER (*Ber.*, 12, 1791—1793).—A mixture of *tetramethylamidodiphenylmethane* and *diphenyldimethylamidosulphone*,  $\text{PhSO}_2\text{C}_6\text{H}_4\text{NMe}_2$ , is formed by the action of dimethylaniline on benzenesulphonic chloride. Hassencamp (*Ber.*, 12, 1275) observed the formation of methyl violet in this reaction, but the chief products, viz., the base and sulphone, appear to have escaped his notice. To obtain the sulphone, the tetramethyldiamidodiphenylmethane, with which it is mixed, is removed by treatment with hydrochloric acid. On recrystallising the residue from alcohol, it is deposited in white needles (m. p. 82°), which are soluble in alcohol, benzene, and ether. The sulphone is decomposed by strong nitric acid, forming three nitro-benzenesulphonic acids and pentanitro-dimethylaniline (m. p. 127°). By the action of paratoluenesulphonic chloride on dimethylaniline, tolyldimethylamidophenylsulphone,  $\text{C}_7\text{H}_7\text{SO}_2\text{C}_6\text{H}_4\text{NMe}_2$ , a blue colouring matter and a base are formed. The sulphone melts at 95°, is soluble in alcohol and ether, and yields a trinitro-derivative on nitration.

W. C. W.

**Action of Sulphonic Chlorides on Amines.** By W. MICHLER and F. SALATHÉ (*Ber.*, 12, 1789—1791).—By the action of  $\alpha$ -naphthalenesulphonic chloride (1 mol.) on dimethylaniline (2 mols.), a blue mass is obtained, which, after saturation with ammonia and distillation in a current of steam, to remove free dimethylaniline, leaves a mixture of *tetramethylamidodiphenylmethane* and  $\alpha$ -naphthyldimethylamidophenylsulphone,  $\text{C}_{10}\text{H}_7\text{SO}_2\text{C}_6\text{H}_4\text{NMe}_2$ . By treating the mixture with dilute hydrochloric acid, the former compound is dissolved; it may be obtained in white plates by precipitation with ammonia and recrystallisation from alcohol. The residue insoluble in hydrochloric acid dissolves in alcohol, and on slow evaporation yields crystals of the sulphone (m. p. 91°), soluble in alcohol and ether, but insoluble in water. This compound is decomposed by fuming hydrochloric acid at 180°, forming aniline, naphthalene, methyl chloride, and sulphuric acid. By the action of strong nitric acid, it is converted into pentanitrodimeethylaniline,  $\text{C}_6(\text{NO}_2)_5\text{NMe}_2$  (m. p. 127°), and  $\beta$ -nitronaphthalenesulphonic acid.  $\beta$ -naphthalenesulphonic chloride and dimethyl-

aniline yield tetramethyldiamidodiphenylmethane, and  $\beta$ -naphthyl-dimethyldiamidophenylsulphone. The latter compound is decomposed by strong nitric acid into pentanitrodiphenylamine, and  $\beta$ -nitronaphthalenesulphonic acid.

W. C. W.

**Dimethylmetatoluidine Derivatives.** By C. WURSTER and C. REIDEL (*Ber.*, 12, 1796—1802).—*Nitrosodimethylmetatoluidine hydrochloride* is deposited on adding a saturated solution of sodium nitrite to a solution of dimethylmetatoluidine in dilute hydrochloric acid. It is sparingly soluble in cold, but dissolves in hot water in presence of hydrochloric acid, and crystallises on cooling in yellow needles.

The free base obtained by decomposing the hydrochloride with sodium carbonate crystallises from ether in green plates or needles (m. p. 92°), soluble in benzene, chloroform, and water. It resembles nitrosodimethylaniline in its reactions.

*Nitrosocresol* is formed, together with dimethylamine when nitrosodimethylmetatoluidine is boiled with soda, and is precipitated on acidifying the alkaline liquid with sulphuric acid. Nitrosocresol crystallises in white needles (m. p. 147—150°), soluble in alcohol, benzene, chloroform, and glacial acetic acid, and sparingly soluble in boiling water and in ether. The acetyl-derivative forms prismatic crystals (m. p. 92°), soluble in alcohol.

*Trinitrocresol* is produced by the action of nitric acid on an acetic acid solution of nitrosocresol.

*Nitrodimethylmetatoluidine* is formed when potassium permanganate is added to an aqueous solution of nitrosodimethylmetatoluidine hydrochloride, and may be extracted from the liquid with ether. It crystallises in long yellow needles (m. p. 84°). The corresponding *dinitro*-derivative is obtained in yellow needle-shaped crystals (m. p. 107°), by adding nitric acid to a solution of dimethylmetatoluidine in glacial acetic acid. If the nitration is carried on with dilute nitric acid, or if the mixture of sulphuric and nitric acids is kept perfectly cold, three nitro-derivatives are obtained, viz., the mono-nitro (m. p. 84°), and two dinitros melting at 107° and 168° respectively. The latter is less soluble in alcohol than the dinitro-compound, melting at 107°.

*Bromodimethylmetatoluidine* melts at 98° and boils at 276°. It is soluble in benzene, aniline, alcohol, and petroleum spirit. On treatment with sodium nitrite, the hydrochloric acid solution yields the nitrosamine in the form of an oily liquid.

*Dimethyltolylenediamine*, obtained by the reduction of nitrosodimethylmetatoluidine with tin and hydrochloric acid, crystallises in white prisms (m. p. 28°), soluble in water, alcohol, ether, and chloroform. The acetyl-derivative melts at 155°.

*Tetramethyltolylenediamine*, prepared by the action of hydrochloric acid and methyl alcohol on the preceding base at 180°, is an oily liquid (b. p. 260°). It combines with methyl iodide to form the compound  $C_6H_3Me(NMe_2)_2(MeI)$ , which crystallises in needles (m. p. 160°). On distillation, it splits up into methyl iodide and the free base.

Ferric chloride produces an intense blue coloration in an aqueous



solution of tetramethyltolylenediamine. Sodium nitrite gives a similar reaction with an acetic acid solution of the base

To estimate the metatoluidine in crude toluidine, the liquid toluidine is first freed from paratoluidine by Bindscheller's process (*Ber.*, 6, 448), converted into hydrochloride, and the orthotoluidine hydrochloride removed by filtration; the filtrate is then evaporated to dryness, converted into dimethyltoluidine, and precipitated as nitroso-dimethylmetatoluidine hydrochloride. W. C. W.

**A Colouring Matter containing Sulphur from Paraphenylenediamine.** By A. KOCH (*Ber.*, 12, 2069—2071).—By treating an acid solution of paraphenylenediamine hydrochloride successively with sulphuretted hydrogen and ferric chloride, a beetle-green crystalline mass is obtained, which has the composition  $C_{24}H_{20}N_6S_2 \cdot 2HCl + 4H_2O$ . This compound is soluble in water and alcohol, forming a violet coloration, which is destroyed by reducing agents and restored by exposure to the air.

The free base,  $C_{24}H_{20}N_6S_2$ , is deposited in dark-brown scales, on the addition of ammonia to the hydrochloride. The base is less soluble than the hydrochloride. The *sulphate*,  $C_{24}H_{20}N_6S_2 \cdot H_2SO_4 + H_2O$ , and the *oxalate*,  $C_{24}H_{20}N_6S_2 \cdot H_2C_2O_4 + 4H_2O$ , form dark-green needles. The *nitrate*,  $C_{24}H_{20}N_6S_2 \cdot 2HNO_3 + 4H_2O$ , crystallises in brown needles. The hydrochloride forms double salts with the chlorides of zinc and mercury, viz.,  $C_{24}H_{20}N_6S_2 \cdot 2HCl \cdot ZnCl_2 + H_2O$  and  $C_{24}H_{20}N_6S_2 \cdot 2HCl \cdot HgCl_2$ .

W. C. W.

**Dimethylparaphenylenediamine Derivatives.** By O. WÜRSTER and R. SENDLER (*Ber.*, 12, 1803—1807).—*Action of Bromine.*—When a 10 per cent. solution of bromine in glacial acetic acid is added to a somewhat more dilute solution of dimethylparaphenylenediamine in the same solvent, a green substance is precipitated, which has the composition  $C_8H_{11}N_2Br$ . The precipitate must be thoroughly washed with glacial acetic acid and with anhydrous ether, and it may be rapidly recrystallised from hot alcohol. From this solvent it is deposited in green scales (m. p. 146°), having a metallic lustre. The aqueous and alcoholic solutions of this substance exhibit an intense red colour, which is destroyed by exposure to the air or by the addition of sulphurous acid.

*Action of Nitrous Acid on Dimethylparaphenylenediamine Ethoxamate.*—On the addition of sodium nitrite to a solution of dimethylparaphenylenediamine ethoxamate in dilute hydrochloric acid, a yellowish-red nitro-product,  $NMe_2 \cdot C_6H_3(NO_2) \cdot NHCO \cdot COOEt$ , collects on the surface. By recrystallisation from acetic acid, it is obtained in red needles (m. p. 152°), freely soluble in benzene, but less soluble in ether and boiling water. On reduction with tin and hydrochloric acid, it yields oxalic acid and dimethyltriamidobenzene [ $NMe_2 : NH_2 : NH_2 = 1 : 3 : 4$ ].

This base crystallises in colourless prisms (m. p. 42—44°, b. p. 298°), soluble in water and petroleum ether. It forms a monoacetyl-derivative, which is deposited from an aqueous solution in transparent prisms or plates, containing 1 mol.  $H_2O$ , which begin to melt at 82°. The anhydrous crystals melt at 153°.

Dimethyltriamidobenzene is also formed by the reduction of Merten's dinitromethylaniline (m. p. 87°), (*Ber.*, 10, 763 and 995).

W. C. W.

**Tetramethylmetaphenylenediamine.** By C. WURSTLE and H. F. MORLEY (*Ber.*, 12, 1814—1815).—On the addition of soda to the product of the action of methyl alcohol and hydrochloric acid at 180° on phenylenediamine, *tetramethylmetaphenylenediamine* separates out as an uncrystallisable oil (b. p. 256° corr.), having a peculiar odour. The hydrochloride forms hygroscopic crystals. The free base unites with methyl iodide to form the compound  $C_6H_4(NMe_2)_2MeI + H_2O$ , which dissolves freely in water, but is less soluble in alcohol. It melts at 192° with decomposition into its constituents. Tetramethylmetaphenylenediamine forms a liquid dibromo-compound, and is converted by the action of nitric acid on its acetic acid solution into trimethylmetaphenylenediamine, a yellow crystalline body (m. p. 132°), soluble in alcohol and in benzene.

W. C. W.

**Action of Oxidising Agents on Tetramethylparaphenylenediamine.** By C. WURSTER and E. SCHOBIG (*Ber.*, 12, 1807—1813).—The unstable blue compound, which is formed by the action of bromine on an acetic acid solution of tetramethylparaphenylenediamine, can be obtained in the form of a microscopic crystalline precipitate by adding ether to the mixture. Its solution in water and in alcohol has an intense blue colour, which is destroyed by sulphurous acid. The substance can also be obtained as ferrocyanide, by adding potassium ferrocyanide to tetramethylparaphenylenediamine sulphate,  $C_{10}H_{16}N_2 + H_4FeC_6 = C_{10}H_{14}N_2.H_4FeC_6 + H_4FeC_6$ .

The ferrocyanide forms blue needle-shaped crystals, having a metallic lustre.

By the action of sodium nitrite on tetramethylparaphenylenediamine, *trimethylphenylenediamine-nitrosamine* is obtained, and a blue colouring matter is produced, which, however, could not be isolated.

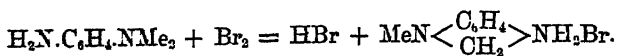
The nitrosamine crystallises in greenish-yellow plates (m. p. 98°), soluble in benzene, chloroform, ether, and hot water. On reduction with tin and hydrochloric acid, it yields trimethylparaphenylenediamine,  $NMe_2.C_6H_4.NHMe$ , an oily liquid (b. p. 265°), sparingly soluble in water. The acetyl-derivative crystallises in prisms containing water (m. p. 78°). The anhydrous crystals melt at 95°.

When an excess of sodium nitrite is added to an acid solution of tetramethylparaphenylenediamine, *nitrotrimethylparaphenylenediamine-nitrosamine*,  $NMe_2.C_6H_3(NMe.NO)(NO_2)$ , separates out in orange-coloured needles (m. p. 87°), soluble in benzene and chloroform, but insoluble in water. On reduction with tin and hydrochloric acid, this compound yields *trimethyltriamidobenzene*,  $NMe_2.C_6H_3(NHMe)NH_2$ , which crystallises in white needles (m. p. 90°, b. p. 294°), soluble in water. Its diacetyl-derivative crystallises in white plates (m. p. 184°).

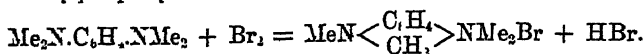
W. C. W.

**Colouring Matters obtained by the Oxidation of Di- and Tetramethylparaphenylenediamine.** By C. WURSTER (*Ber.*, 12, 2071—2072).—The author proposes to represent the formation of the red and blue colouring matters obtained by the action of oxidising

agents on di- and tetra-methylparaphenylenediamine respectively (*Ber.*, 12, 1803 and 1807), by the following equations:—



Dimethylparaphenylenediamine



Tetramethylphenylenediamine

W. C. W.

**Action of Nitrous Acid on Mono- and Diethylenediphenyldiamine.** By H. F. MORLEY (*Ber.*, 12, 1793—1796).—The ethylenediphenyldiamine used in these experiments was prepared by warming a mixture of ethylene bromide (1 mol.) with aniline (4 mols.) in a large flask provided with an upright condenser. An active reaction takes place, and on cooling, the contents of the flask solidify. Aniline hydrobromide is dissolved out on heating the product with water, leaving the diamine, which may be obtained in glistening scales (m. p. 63°), by recrystallisation from dilute alcohol.

*Ethylenediphenyldinitrosamine* separates out as a yellowish-green precipitate on the addition of sodium nitrite to a solution of ethylenediphenyldiamine in dilute hydrochloric acid. On recrystallisation from acetic acid, it is obtained in scales (m. p. 157°), insoluble in water, ether, and cold alcohol.

*Dinitrosodiethylenediphenyldiamine*, obtained as a yellowish-green precipitate, yields, on reduction with tin and hydrochloric acid, *diethylenediphenylenetetramine*,  $\text{NH}_2.\text{C}_6\text{H}_4.\text{N}:(\text{C}_6\text{H}_4)_2:\text{N}.\text{C}_6\text{H}_4.\text{NH}_2$ . This base crystallises in glistening scales (m. p. 221°), sparingly soluble in ether, alcohol, and benzene. Ferric chloride produces a violet coloration in solutions of its salts.

W. C. W.

**Ethereal Oil of *Origanum Hirtum* and Cretan Oil of *Marjoram*.** By E. JAHNS (*Arch. Pharm.* [3], 15, 1—19).—The essential oil of *Origanum hirtum* has an aromatic thyme-like odour, neutral reaction, and a sp. gr. of 0.951 at 15°; it is feebly levorotatory (100 mm. producing a rotation of -0.40°). When treated with a 15 per cent. solution of sodium carbonate, it dissolves, and on diluting the clear brown solution with warm water, the greater portion of the hydrocarbon separates, leaving a phenol in solution. This phenol,  $\text{C}_{10}\text{H}_{14}\text{O}$ , which amounts to half the oil, was proved to be carvacrol, as on chlorination it yielded a chlorcymene,  $\text{CH}_3:\text{Cl}:\text{C}_6\text{H}_3 = [1:2:4]$ , which on oxidation yielded chlorparatoluic acid. The sodium, potassium, barium, calcium, magnesium, and silver salts of carvacrol sulphonic acid are described: the barium salt crystallises with  $5\text{H}_2\text{O}$ , and appears to be different from that described by Pott, which has the composition  $(\text{C}_{10}\text{H}_{13}\text{O}.\text{SO}_3)_2\text{Ba}$ . The sulphonic acid, when distilled with manganese dioxide and sulphuric acid, yields thymoquinone. The melting point of the carvacrol, 1.5—2°, does not appear quite to agree with those obtained by other investigators. It yields ordinary cymene when treated with phosphorus trisulphide. In the acid solution, from which the carvacrol was separated, there appeared to be a small quantity of

a volatile acid, which reduced silver solution (formic acid?). That portion of the oil which was separated by the addition of water to the soda solution appeared to be a mixture of terpenes. Submitted to distillation, a third passed over at 170—180°; another third at 180—190°; the remainder at 250°. Finally, the portion 172—176° (a quarter of the whole), which had an odour of oil of lemons, yielded, when treated with sulphuric acid, a very small quantity of cymenesulphonic acid. The results of the investigation are, that oil of *Origanum hirtum* consists of 50—60 per cent. of carvacrol, the rest being a mixture of terpenes. There also appears to be a small quantity of a phenol which gives a reddish-violet colour with ferric chloride. This oil is the only natural source of carvacrol, except the oil of *Thymus serpyllum*, where it is present to the amount of 3 per cent. Oil of *Origanum Onites* obtained from various sources, which had a deeper and more red-brown colour than that of *Origanum hirtum*, was also remarkable for the large amount of carvacrol which it contained. All the specimens contained the phenol (1—2 per cent.) which is coloured violet by ferric chloride. An oil prepared in France, having the name *Ol. origani Gull.*, contains no carvacrol; it should therefore be distinguished from Cretan oil of marjoram, this name being applied only to that from Greece and Asia Minor. Tests for identification which can be applied are: mixing with 90 per cent. alcohol in all proportions; production of a green or violet colour by ferric chloride; violent reaction with phosphorus pentachloride, accompanied by evolution of hydrochloric acid gas, followed by the production of a bluish-red coloration. Those oils which contain 50 per cent. or more of carvacrol will produce a clear mixture with half their volume of a 15 per cent. soda solution.

E. W. P.

**Resorcinol and Orcinol Derivatives.** By V. MINZ and G. ZETTER (*Ber.*, 12, 2035—2049).—The best yield of trinitroresorcinol or styphnic acid is obtained by nitrating resorcinoldisulphonic acid. For this purpose finely powdered resorcinol is added in small portions at a time, to five times its weight of strong sulphuric acid at 40°; the clear red solution is heated at 100°, when it crystallises, forming a thick paste. The acid mixture is poured into cold water, and nitric acid diluted with 10 per cent. of water is slowly added, care being taken to avoid any rise of temperature. Towards the end of the operation fuming nitric acid is employed; at least twice the theoretical amount of nitric acid must be used for nitration. The product of the reaction is left at rest for 12 hours, and then poured into twice its volume of cold water, when trinitroresorcinol separates out as a granular crystalline mass (m. p. 174·5°).

Trinitro-orcinol can be prepared by a similar method, but the yield is not so good as in the case of trinitroresorcinol, only about 60 per cent. of the theoretical yield being obtained. The mixture of orcinol and sulphuric acid is heated on a water-bath, but in order to complete the reaction, the temperature must be raised to 150°. In the process of nitration, it is necessary to use rather dilute nitric acid, and to cool the mixture with ice. Trinitro-orcinol crystallises in long yellow needles (m. p. 163·5°).

*Trihydroxybenzoquinone* is formed by the action of dilute hydrochloric acid (8—10 per cent. solution) at 140—150° on the hydrochloride of amidodi-imidoresorcinol, prepared by the addition of ferric chloride to a solution of triamidoresorcinol hydrochloride (Schreder, *Annalen*, 158, 244). The crude product may be purified by solution in soda, and reprecipitation by hydrochloric acid. Trihydroxybenzoquinone exists as a dark, almost black, amorphous powder, and also in the form of dark crystalline scales, which are sparingly soluble in the usual solvents. The ammoniacal solution of this substance produces dark coloured precipitates with salts of the heavy metals and alkaline earth-metals, e.g.,  $(C_6H_3O_3)_2(BaO_2)_3$ ;  $C_6H_3O_3(AgO)_3$ .

Acetic chloride attacks trihydroxybenzoquinone at the ordinary temperature, forming *triacetoxyquinone*,  $C_6H_3O_3(OAc)_3$ , which is deposited from a solution in hot acetic acid in small crystalline scales. The corresponding tribenzoyl compound,  $C_6H_3O_3(OBz)_3$ , has not yet been obtained in a crystalline state. *Bromotrihydroxyquinone*,  $C_6Br_3(OH)_3$ , prepared by warming a solution of trihydroxybenzoquinone in acetic acid with bromine, is a brown uncrystallisable powder, sparingly soluble in alcohol. It forms insoluble compounds with the heavy metals, e.g.,  $Pb_2(C_6Br_3O_3)_2$ . *Trihydroxytoluquinone*,  $C_6Me_3(OH)_3$ , is deposited in dark-coloured crystals when amidodiimido-resorcinol hydrochloride is heated with a 10 per cent. solution of hydrochloric acid at 140—150°. The crude product is purified by conversion into the triacetyl derivative,  $C_6Me_3(OAc)_3$ , a yellow lustrous crystalline powder, soluble in hot alcohol. When treated with a solution of soda, this yields a brown liquid, from which pure trihydroxytoluquinone is precipitated on the addition of an acid.

This toluquinone dissolves in hot alcohol, forming a dark cherry-coloured solution. It forms with calcium, barium, and silver dark-coloured precipitates, which are insoluble in water.

*Trinitroresorcinol* dissolves in fuming sulphuric acid, but is not reprecipitated on dilution with water. When air containing bromine vapour is passed through an aqueous solution of monosodium trinitroresorcinol,  $C_6H(NO_2)_3ONa.OH$ , a mixture of bromopierin and nitrodibromethylene,  $CBBr_2:CH.NO_2$ , is formed. The latter on recrystallisation from chloroform is deposited in transparent, six-sided rhombic prisms (m. p. 112°), soluble in alcohol, ether, carbon bisulphide, and benzene. The solution stains the skin red. The addition of alkalis to the alcoholic solution produces a transient red coloration; nitrate of silver and lead acetate throw down from the red liquid a red precipitate, which rapidly changes to the corresponding metallic bromide.

W. C. W.

**Compounds of the Hydrobenzoïns and Stilbene. Series II.** By T. ZINCKE (*Annalen*, 198, 115—141).—This is an important paper on a probable case of true physical isomerism. It has been previously shown (*Annalen*, 182, 241; *Chem. Soc. J.*, 1875, 453), that the two diatomic alcohols obtained from stilbene,  $C_6H_5.CH:CH.C_6H_5$ , by the addition of bromine, and conversion of the bromide into the acetate or benzoate, and subsequent saponification, are respectively identical with the hydro- and isohydro-benzoïn obtained from benzaldehyde by

the action of hydrogenising agents. Although any two of the following formulæ: I.  $\text{CHPh}(\text{OH})\cdot\text{CHPh}(\text{OH})$ ; II.  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})_2\text{Ph}$ ; III.  $\text{CHPh}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2(\text{OH})$ , for these two alcohols would explain their isomerism, and *simultaneous formation* from stilbene or benzaldehyde, yet such formulæ would not agree with other reactions of the alcohols. So far, it has not been possible to prove the existence of two isomeric dibromides in crude stilbene bromide.

On oxidation with chromic mixture, both alcohols behave exactly alike, and give first benzaldehyde and then benzoic acid, together with small quantities of benzophenone, the formation of the latter being due to a secondary reaction. These facts show that the third of the above formulæ is inadmissible for either alcohol.

By oxidation with nitric acid, hydrobenzoïn gives first benzoïn,  $\text{Ph}\cdot\text{CO}\cdot\text{CHPh}(\text{OH})$ , and then benzil  $\text{Ph}\cdot\text{CO}\cdot\text{COPh}$ , from which it follows that it has the constitution represented by formula I. Ammann and Fittig (*Annalen*, 168, 75) found that isohydrobenzoïn on oxidation with nitric acid, gave only resinous products; the author, however, finds that this oxidation gives first a substance which crystallises in monoclinic crystals (m. p.  $98^\circ$ ), and then a body crystallising in yellow needles (m. p.  $78-81^\circ$ ). Both these compounds are still under investigation. From the above-mentioned results obtained by oxidation, it follows that the only possible formulæ for hydro- and isohydrobenzoïn are I and II respectively, and the latter on oxidation with nitric acid would give, first,  $\text{CPh}(\text{OH})_2\cdot\text{COPh}$ , or  $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , and then benzil. The author, however, considers that the oxidation product (m. p.  $98^\circ$ ) is a physical isomeride of benzoïn, and the product (m. p.  $78-81^\circ$ ) the corresponding physical isomeride of benzil: for in several subsequent experiments on the oxidation of isohydrobenzoïn with nitric acid, these two bodies (m. p.  $98^\circ$  and  $78-81^\circ$ ) were not obtained, but only *ordinary benzoïn and benzil*, the only difference between hydro- and isohydrobenzoïn in this respect being that with the latter, the crude products were always resinous.

On treatment with phosphorus pentabromide, both hydro- and isohydrobenzoïn give exactly the same dibromide (m. p.  $237^\circ$ ), which, with silver acetate or benzoate, gives in both cases the hydro- and isohydrobenzoate, and these on saponification yield again hydro- and isohydrobenzoïn respectively, exactly as stilbene bromide does.

By the action of phosphorus, pentachloride hydrobenzoïn gives two isomeric dichlorides,  $\text{C}_{14}\text{H}_{12}\text{Cl}_2$  (m. p.  $192^\circ$  and  $94^\circ$ ), whilst isohydrobenzoïn gives only one (m. p.  $192^\circ$ ) which is identical with the former of the two just mentioned.

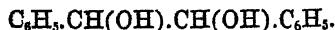
*$\alpha$ -Hydrobenzoïn dichloride*,  $\text{C}_{14}\text{H}_{12}\text{Cl}_2$ , already described by Ammann and Fittig (*loc. cit.*), crystallises in needles or prisms (m. p.  $192^\circ$ ), which are sparingly soluble in alcohol, but easily soluble in toluene, ether, and chloroform, and sublime in plates.

*$\beta$ -Hydrobenzoïn (or isohydrobenzoïn) dichloride*,  $\text{C}_{14}\text{H}_{12}\text{Cl}_2$ , differs greatly from the preceding compound in physical, but has exactly the same chemical properties. It dissolves easily in most solvents, and crystallises in four- or six-sided plates (m. p.  $94^\circ$ ), and sublimes without decomposition. When heated, both the  $\alpha$ - and  $\beta$ -chlorides undergo a most remarkable change as regards melting point, in such a way that

they both apparently give a third dichloride (m. p.  $160^{\circ}$ ), which is more stable than the other two. The investigation of the anhydrides of hydro- and isohydro-benzoïn has also proved the existence of a third dichloride (m. p.  $153^{\circ}$ ). The dichloride (m. p.  $160^{\circ}$ ) is, however, probably a mixture of the  $\alpha$ - and  $\beta$ -chlorides, since on crystallisation it may be separated into the  $\alpha$ - and  $\beta$ -dichlorides.

Both hydro- and isohydro-benzoïn, when treated with phosphorus trichloride, give only one dichloride, viz., that melting at  $192^{\circ}$ . By conversion into the acetate, and subsequent saponification and crystallisation from hot water,  $\alpha$ -hydrobenzoïn chloride (m. p.  $192^{\circ}$ ) is converted almost wholly into isohydrobenzoïn, together with small quantities of hydrobenzoïn. Under similar circumstances,  $\beta$ -hydrobenzoïn (or isohydrobenzoïn) dichloride (m. p.  $94^{\circ}$ ) gives the same results. If, however, for the conversion of these chlorides into the alcohols, silver benzoate is used in place of the acetate, then both  $\alpha$ - and  $\beta$ -chloride give chiefly hydrobenzoïn, together with small quantities of isohydrobenzoïn.

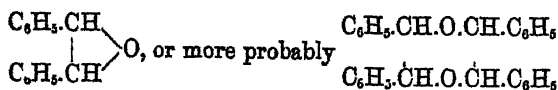
The author considers that the above facts cannot be explained by a different grouping of the atoms, and that hydro- and isohydro-benzoïn must have identically the same chemical molecule,



In other words they are true physical isomerides.

T. C.

**Compounds obtained from Hydro- and Isohydro-benzoïn by the Action of Dilute Sulphuric Acid.** By A. BREUER and T. ZINCKE (*Annalen*, 198, 141—190).—This is a continuation of Zincke's investigation with regard to the isomerism of hydro- and isohydro-benzoïn (see preceding Abstract). The authors advance the following general rule:—"On abstraction of water, which can be effected by various reagents, all diatomic alcohols, containing the OH-groups attached to two neighbouring carbon atoms, give first oxides (anhydrides or ethers) without any intramolecular changes, and then by further action of the reagent, ketones, or aldehydes, or both." Both hydro- and isohydro-benzoïn must be considered as aldehyde pinacones, thus:— $\text{C}_6\text{H}_5.\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{C}_6\text{H}_5$ . By the action of dilute sulphuric acid, zinc chloride, or hydrochloric acid both give two compounds, the one crystalline and the other liquid. With hydrobenzoïn the yield is 20 to 25 per cent. of the former, and 50 to 60 per cent. of the latter, whereas with isohydrobenzoïn the reverse is the case. The former compounds are *anhydrides*—



and although chemically identical, they are physically (in melting point and crystalline form) different. The liquid compounds appear to be identical both chemically and physically; they are *aldehydes*,  $\text{CHPh}_2.\text{COH}$ , and their formation therefore can only be explained by intramolecular transference of the  $\text{C}_6\text{H}_5$ -group. By the continued

action of the reagent, the above crystalline compounds are also converted into this aldehyde, and by oxidation both give the same product,  $C_{22}H_{22}O_3$ .

Convenient methods of preparing hydro- and isohydro-benzoin are described. Benzoin by the action of sodium amalgam in dilute alcoholic solution gives not only hydrobenzoin (33 per cent.) but also small quantities of isohydrobenzoin (1 per cent.).

*Hydrobenzoin anhydride*,  $C_{14}H_{12}O$ , forms monoclinic crystals (m. p.  $132^\circ$ ), which are easily soluble in hot alcohol, benzene, chloroform, and glacial acetic acid, and but sparingly soluble in light petroleum. It is not volatile in steam.

*Isohydrobenzoin anhydride*,  $C_{14}H_{12}O$ , forms brilliant monoclinic crystals (m. p.  $102^\circ$ ), very similar in form to gypsum; these become dull on keeping. It is more soluble in alcohol than the hydrobenzoin-compound, but behaves in a similar manner towards other solvents.

Neither anhydride is attacked by sodium amalgam; both give stilbene bromide on treatment with bromine, and both when heated in sealed tubes at  $260^\circ$  yield benzaldehyde and stilbene,  $2C_{14}H_{12}O = 2C_7H_6O + C_{14}H_{12}$ . Heated with benzoic acid at  $240^\circ$ , the hydrobenzoin anhydride gives very small quantities of hydrobenzoin benzoate (m. p.  $242^\circ$ ), whilst the iso-compound gives only traces of isohydrobenzoin. Treated with acetic anhydride in sealed tubes, both compounds yield small quantities of hydro- and isohydro-benzoin. Heated with acetic acid at  $165^\circ$ , the hydrobenzoin anhydride is converted into hydrobenzoin acetate, whilst the iso-compound is but slightly attacked even at  $250^\circ$ , and besides benzaldehyde and stilbene gives only small quantities of isohydrobenzoin.

On treating hydrobenzoin anhydride with phosphorus pentachloride at  $130^\circ$ , the same chloride,  $C_{14}H_{12}Cl_2$  (m. p.  $192^\circ$ ), is obtained as from hydrobenzoin itself, together with but a small quantity of resin, and none of the chloride of melting point  $94^\circ$ . Isohydrobenzoin anhydride under similar circumstances gives, besides the chloride (m. p.  $192^\circ$ ), also a resinous body ( $C_{22}H_{22}OCl_2$ , m. p.  $87^\circ$  ?), which was far more abundant than in the case of the hydrobenzoin compound. On saponification, this resin gave hydro- and isohydro-benzoin; by recrystallisation, it was converted into the compound  $C_{22}H_{22}OCl$  (m. p.  $153^\circ$ ), which is more soluble in alcohol than the dichloride (m. p.  $192^\circ$ ).

Both anhydrides on oxidation give a compound,  $C_{22}H_{22}O_3$ , together with small quantities of benzoic acid and other products, amongst which there is one crystallising in needles or plates (m. p.  $144^\circ$ ), which appears to be a reduction-product of the compound  $C_{22}H_{22}O_3$ . This latter substance is easily soluble in benzene and chloroform, and but sparingly soluble in light petroleum; it is also difficultly soluble in cold, but more easily soluble in hot alcohol, and crystallises in needles or plates (m. p.  $155^\circ$ ). The formation of this body by the oxidation of hydro- and isohydro-benzoin anhydrides seems to show that the formula of these latter is more probably  $C_{22}H_{22}O_3$  than  $C_{14}H_{12}O$ . On oxidation with chromic and acetic acids, it gives neither benzoic acid nor benzophenone, but a new compound ( $C_{22}H_{22}O_4$  or  $C_{22}H_{22}O_3$  ?), which crystallises in plates (m. p.  $98^\circ$ ). On reduction with phosphorus and hydriodic acid, the compound  $C_{22}H_{22}O_3$  gives dibenzyl



(m. p.  $52^{\circ}$ ), and a substance,  $C_{11}H_{10}O_2$ , crystallising in needles (m. p.  $144^{\circ}$ ), sparingly soluble in water, but easily soluble in alcohol, ether, and benzene, and which on further oxidation give chiefly benzophenone.

By reduction with phosphorus and hydriodic acid, hydro- and isohydro-benzoin anhydrides both yield dibenzyl, together with a small quantity of an oil, thus showing that they are both derivatives of the same hydrocarbon; the oil on oxidation gave benzophenone. Diphenylaldehyde is obtained on heating either anhydride with dilute sulphuric acid at  $210^{\circ}$ : hydrobenzoin chloride (m. p.  $182^{\circ}$ ), together with diphenylaldehyde, is obtained by heating the anhydrides with strong hydrochloric acid at  $170^{\circ}$ . Benzoic chloride converts both anhydrides into hydrobenzoin chlorides (m. p.  $192^{\circ}$ ). All the above reactions show that the two anhydrides are almost completely identical, and that the difference between them is probably of the same kind as that between the corresponding alcohols. These results also on the whole point to the formula,  $C_{12}H_{10}O_2$ , for the anhydrides, rather than to the simpler formula,  $C_{14}H_{12}O$ .

It has not yet been possible to decide finally whether the aldehydes obtained from hydro- and isohydro-benzoin, by the action of dilute sulphuric acid, are absolutely identical both physically and chemically, but it is very probable that they are.

Both these aldehydes give benzophenone on oxidation, and not diphenylacetic acid, and only by treatment with alcoholic potash was it possible to convert them into the latter compound; even then, the chief products were benzhydrol and diphenylmethane. These aldehydes which the authors consider on the whole to be identical, have the composition of a *diphenyl-aldehyde*,  $C_{14}H_{12}O$ ; the product is a colourless oil, heavier than water, and insoluble therein, but easily soluble in ether, alcohol, benzene, and chloroform. It boils at  $315^{\circ}$  with slight decomposition. On keeping for many weeks it yields formic acid and benzophenone, and gradually becomes crystalline. The crystals from the hydrobenzoin aldehyde melt at  $213^{\circ}$ , and those from the iso-compound at  $167^{\circ}$ . In a second experiment, however, the hydrobenzoin aldehyde also gave crystals melting at  $167^{\circ}$ , and not at  $213^{\circ}$ ; the change which here takes place is probably as follows:—  
 $2(C_6H_5)_2CH.CO.H + O_2 = (C_6H_5)_2C : C(C_6H_5)_2 + 2CH_2O_2$ , and  
 $(C_6H_5)_2CH.CO.H + O_2 = (C_6H_5)_2CO + CH_2O_2$ . Both the crystalline bodies on oxidation give benzophenones, and by treating the one melting at  $167^{\circ}$  with acetic chloride, a crystalline body (m. p.  $125$ — $130^{\circ}$ ) is obtained.  
 T. C.

**Physical Isomerism, with Special Reference to Hydro- and Isohydro-benzoin.** By T. ZINCKE (*Annalen*, 198, 191—203).—In this paper the theories which have been proposed by Laubenheimer (*Ber.*, 9, 766), Lehmann (*Zeits. f. Krystallographie*, 1, 110), and Van't Hoff, to account for physical isomerism, are severally discussed, and the author arrives at the conclusion that the physical isomerism in the case of the hydrobenzoins cannot be satisfactorily explained by means of any of them.  
 T. C.

**Orthobrombenzoic Acid.** By M. REAUS (*Annalen*, 198, 99—

114).—This acid is best prepared by oxidising liquid bromotoluene with potassium permanganate. It crystallises from hot water in colourless silky needles (m. p. = 150°; 148°, Zincke, *Ber.*, 7, 1502; 138°, Richter, *Ber.*, 4, 459), which are sparingly soluble in cold water, but far more soluble than either the meta- or para-derivatives, from which it is still further distinguished by being little or not at all volatile in steam. It is easily soluble in alcohol, ether, and chloroform. When fused with potash it yields parahydroxybenzoic acid (?), and but a trace of salicylic acid. The salts of the alkalis and alkaline earths are easily soluble in water, and those of the heavy metals but slightly soluble. The following salts were prepared and examined:—

The potassium salt,  $C_7H_4BrO_2 \cdot K \cdot 2H_2O$  (m. p. 245°); sodium salt,  $C_7H_4BrO_2 \cdot Na$ ; barium salt,  $Ba(C_7H_4BrO_2)_2 \cdot 2C_2H_5O$  (from alcohol); calcium salt,  $(C_7H_4BrO_2)_2 \cdot Ca \cdot 3H_2O$ ; zinc salt,  $(C_7H_4BrO_2)_2 \cdot Zn$ ; neutral copper salt,  $(C_7H_4BrO_2)_2 \cdot Cu \cdot H_2O$  (m. p. = 257° with decomposition) are crystalline, whilst the basic copper salt,  $C_7H_4BrO_2 \cdot Cu \cdot OH$ , silver salt and lead salt,  $(C_7H_4BrO_2)_2 \cdot Pb \cdot C_2H_5O$  (m. p. = 176—180°), are amorphous precipitates.

Methyl orthobromobenzoate,  $C_7H_4BrO_2 \cdot Me$ , is obtained as a colourless liquid (b. p. = 246°) by the action of methyl iodide on the silver salts.

Ethyl orthobromobenzoate,  $C_7H_4BrO_2$ , is a colourless liquid (b. p. = 254°).

Nitro-orthobromobenzoic acid,  $C_6H_3Br(NO_2) \cdot COOH$ , is obtained by dissolving the bromobenzoic acid in cold fuming nitric acid, and is identical with the acid previously prepared by Burghardt (*Ber.*, 8, 560). It crystallises from hot water in brilliant needles (m. p. = 180°), which are sparingly soluble in cold, but more easily in hot water, and very easily in alcohol, ether, and chloroform. The barium salt  $[C_6H_3Br(NO_2)O_2]_2 \cdot Ba \cdot 5\frac{1}{2}H_2O$ , crystallising in needles or prisms, and the silver salt were prepared. Ethyl nitro-orthobromobenzoate,  $C_6H_3Br(NO_2) \cdot COOEt$ , crystallises in needles (m. p. = 66°), which are insoluble in water, but easily soluble in alcohol and in ether.

That nitro-orthobromobenzoic acid has the constitution—



was proved by converting it (by treatment with aqueous ammonia) into nitro-amidobenzoic acid (m. p. 270°), which is identical with that obtained by Waltenberg (*Ber.*, 8, 1217) from ethyl paranitrosalicylate. Now Kruse has shown that the nitro-group of this acid must be in the meta-position in reference to the carboxyl-group, and hence the acid must have one of the two following constitutions:—



but the fact that nitro-orthobromobenzoic acid gives paranitraniline (m. p. 148°) on treatment with alcoholic ammonia proves that the latter of these is the true one. T. C.

Paranitrophenylacetic Acid. By T. MAXWELL (*Ber.*, 12, 1764—1768).—The nitrophenylacetic acid (m. p. 114°) which Radziszewski

(*Ber.*, 2, 209 and 3, 648) obtained by nitrating phenylacetic acid is not a definite compound, but a mixture of para- and ortho-nitrophenylacetic acids, which cannot be separated by recrystallisation from alcohol. The mixed acids (m. p.  $114^{\circ}$ ) were converted into methyl salts and dissolved in boiling light petroleum, when pure methyl paranitrophenylacetate was deposited in long glistening needles (m. p.  $54^{\circ}$ ), leaving a mixture of methyl ortho- and para-nitrophenylacetates in the mother-liquor.

The paranitro acid crystallises in silky needles (m. p.  $152^{\circ}$ ) soluble in alcohol, ether, and benzene. On oxidation, it yields paranitrobenzoic acid (m. p.  $235^{\circ}$ ), and on reduction with tin and hydrochloric acid, amidophenylacetic acid.

*Barium paranitrophenylacetate* crystallises in yellow anhydrous needles, freely soluble in water.

The zinc salt forms needles containing one mol.  $H_2O$ , the silver salt also forms colourless needles, which are sparingly soluble in cold water. The salts of the alkalis are very soluble. *Methyl paranitrophenylacetate* melts at  $54^{\circ}$ , and is soluble in alcohol, benzene, and ether. The addition of a few drops of alcoholic potash produces a beautiful violet coloration in the alcoholic solution of this substance.

The ethyl salt crystallises in thin plates (m. p.  $65.5^{\circ}$ ) soluble in alcohol and ether. W. C. W.

**Polymerised Non-saturated Acids.** By R. FITTIG (*Ber.*, 12, 1739—1744).—When methacrylic acid is heated at  $130^{\circ}$  in sealed tubes, it is converted into a polymeric modification in the form of a white hard mass resembling porcelain in appearance. This substance does not dissolve in water, but slowly unites with it, forming a clear transparent liquid, from which the polymeride can be separated as a colourless gelatinous mass, by filtration. Attempts to ascertain the constitution of this compound have been unsuccessful, since it is either not acted on by treatment with oxidising agents, or else completely destroyed.

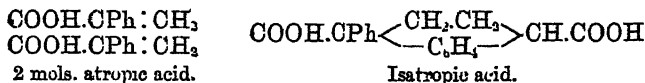
*Isatrylic acid* obtained by heating atropic acid at a temperature above its melting point, is converted into anthraquinone and ortho-benzoylbenzoic acid,  $Ph.CO.C_6H_4.COOH$  (b. p.  $127^{\circ}$ ) when chromic acid is added in small portions at a time, to an acetic acid solution of the acid.

By the action of sulphuric acid on isatropic acid at a temperature not exceeding  $50^{\circ}$ , carbonic oxide and a monobasic acid,  $C_{17}H_{14}O_2$ , are produced. The acid is deposited from an alcoholic solution in colourless plates which melt at  $156^{\circ}$ , and decompose on distillation into carbonic anhydride and a liquid hydrocarbon,  $C_{16}H_{14}$  (b. p.  $320^{\circ}$ ). If the mixture of sulphuric and isatropic acids is heated at  $100^{\circ}$ , a sulphonic acid,  $C_{16}H_{13}SO_3$  or  $C_{15}H_{12}SO_3$  is formed. This compound, which can also be prepared by the action of sulphuric acid on the new acid,  $C_{17}H_{14}O_2$ , is insoluble in water. It dissolves in acetic acid and crystallises from this solution in transparent prisms, which melt with decomposition at  $258^{\circ}$ .

The solution of the sulphonic acid in water containing sodium carbonate may be preserved in the dark without undergoing any altera-

tion, but on exposure to the light, the liquid rapidly becomes turbid, and deposits a yellow precipitate (m. p. 193°), soluble in alcohol.

Isatropic acid is decomposed by distillation, yielding (1) a hydrocarbon,  $C_{16}H_{14}$  (b. p. 320°); (2) a monobasic acid,  $C_{17}H_{14}O_2$ , crystallising in prisms (m. p. 163°), which is not identical with the previously described acid of the same composition; (3) a soluble acid, probably  $C_{17}H_{16}O_2$ , not yet obtained in the crystalline state. From the preceding observations, the author concludes that the conversion of atropic into isatropic acid, may be best represented thus:—



In the preparation of isatropic acid by the long-continued boiling of atropic acid with water, a second polymeride is formed. On recrystallising the product from acetic acid, the new acid is found in the mother-liquor, from which it can be obtained in plates (m. p. 205°). It is converted into isatropic acid (m. p. 237°) by exposure to a temperature of 220° for some time.

*Cinnamic acid* can easily be polymerised, but the dibasic acid,  $C_{16}H_{16}O_4$ , corresponding to isatropic acid, has not yet been isolated. The monobasic acid,  $C_{17}H_{16}O_2$ , is formed by boiling a solution of cinnamic acid in 5 parts of glacial acetic acid with  $\frac{1}{4}$  its volume of sulphuric acid, or by treating cinnamic acid with sulphuric acid diluted with  $1\frac{1}{2}$  times its volume of water. In the latter method, the hydrocarbon,  $C_{16}H_{16}$  (b. p. 310—312°), described by Erlenmeyer as *distyrene*, and also investigated by Kratau (*Ber.*, 11, 1260), is obtained as a by-product. The acid,  $C_{17}H_{16}O_2$ , is a colourless amorphous substance, insoluble in water, but dissolved by ether, alcohol, and acetic acid. Its calcium salt is insoluble in hot water.

W. C. W.

**The Isomeric Nitrosalicylic Acids.** By H. SCHIFF and F. MASINO (*Gazzetta*, 9, 318—327).—In the first part of the paper the authors give an account of the various researches which have been made on the nitrosalicylic acid obtained by the action of dilute nitric acid on indigo, hitherto supposed to be homogeneous, and the nitrosalicylic acid from salicin or salicylic acid, which has been shown to be a mixture of two isomerides, melting at 125° (144° when anhydrous) and at 228° respectively. The authors find, however, that the nitrosalicylic acid from indigo may also be separated into two portions, one melting at 125° and the other at 228°. This is effected by first converting the crude acid into ammonium salt, and after separating the resin, boiling the solution with excess of baryta-water. The barium salts thus obtained are then separated by fractional crystallisation, the one containing the acid of melting point 228° being least soluble. According to the authors, the acid which forms anhydrous crystals (m. p. 228°) has the constitution  $[\text{COOH:OH:NO}_2 = 1:2:5]$ , whilst the acid crystallising with one  $H_2O$  (m. p. 125°) has the constitution  $[1:2:3]$ . From these results, it is evident that the acid obtained from indigo, like that from salicin or salicylic acid, is a mixture of two isomerides.

C. E. G.

**Artificial Tannin.** By P. FREDA (*Gazzetta*, 9, 327—332).—The author has repeated the experiments described by Schiff (*Gazzetta*, 8, 203, and this *Journal*, Abst., 1879, 646), but obtains totally different results, all tending to confirm the conclusion at which he had arrived, that the supposed digallic acid or artificial tannin of Schiff, obtained by the action of arsenic acid on gallic acid, is merely an arsenical compound of gallic acid. He has analysed the precipitate formed in quinine solution, and finds that it contains as much as 7—8 per cent. of arsenic in different specimens; when the arsenic is removed, none of the tannin reactions could be observed. The author's experiments show that arsenic acid, whether in aqueous or alcohol solution, does not transform gallic acid into digallic acid, but into an arsenical compound, which has some properties in common with tannin, and that when this compound is freed from arsenic by hydrogen sulphide, gallic acid is regenerated. The author has observed also that the melting point of gallic acid is much lower (210°) when it is gradually heated than when it is rapidly heated (240—252°), probably owing to incipient decomposition. C. E. G.

**Amidobenzenedisulphonic Acids.** By O. ZANDER (*Annalen*, 198, 1—29).—(1.) *Paramidobenzenedisulphonic* or *disulphumic acid*,  $C_6H_5NH_2(SO_3H)_2 \cdot 2H_2O$  [ $SO_3H : NH_2 = 1 : 3 : 4$ ], is obtained by the action of fuming sulphuric acid on paramidobenzenesulphonic acid (sulphanilic acid), and is also found in the mother-liquor left in the preparation of sulphanilic acid. It crystallises in small reddish needles, which dissolve readily in water and alcohol, but not in ether. Bromine throws down tribromaniline from an aqueous solution of the acid. It forms normal and acid salts, the former of which dissolve easily in water, the latter less readily, whilst both are insoluble in alcohol. *Normal ammonium paramidobenzenedisulphonate*,



forms small transparent yellowish hexagonal prisms. The *acid salt*,  $C_6H_5(NH_2)(SO_3H) \cdot SO_3NH_4 \cdot 2H_2O$ , crystallises in large white needles, which become reddish when exposed to the air.

The *normal potassium salt*,  $C_6H_5NH_2(SO_3K)_2 \cdot H_2O$ , forms very hard yellowish nodules, and the acid salt white silky needles.

The salts of calcium, barium, lead, and silver, resemble those described, except that the acid calcium salt and both the silver salts are anhydrous.

*Diazoparabenzenedisulphonic acid*,  $C_6H_5(SO_3H) : N_2SO_3$ , may be obtained by the action of nitrous acid on an alcoholic solution of the amidodisulphonic acid, but a better method of preparing it is by nitration of an acid salt.

The diazoparabenzenedisulphonates dissolve in cold water, and are precipitated by alcohol from the aqueous solution. They do not explode by percussion. Heated on platinum foil they burn brightly, leaving a carbonaceous residue. When heated with alcohol, or boiled with water or with hydrobromic acid, they yield benzenedisulphonates, phenoldisulphonates, and bromobenzenedisulphonates.

*Ammonium diazoparabenzenedisulphonate*,  $C_6H_5(NH_4SO_3) : N_2SO_3$ ,

prepared by passing nitrous acid into an ice-cold concentrated solution of hydrogen-ammonium paramidobenzenedisulphonate, forms white needles. The *potassium* salt obtained in a similar manner is also anhydrous. The *barium* and *calcium* salts contain 2, the *lead* salt 3 mols. of water of crystallisation.

*Metabenzenedisulphonic acid* [ $\text{SO}_3\text{H} : \text{SO}_3\text{H} = 1 : 3$ ].—When calcium diazoparabenzenedisulphonate is heated with alcohol under pressure, nitrogen is evolved, and the free benzenedisulphonic acid is found in the solution (this Journal, 1878, Abst., 409).

*Bromobenzenedisulphonic acid* [ $\text{SO}_3\text{H} : \text{SO}_3\text{H} : \text{Br} = 1 : 3 : 4$ ], is obtained by heating the salts of the diazodisulphonic acid with hydrobromic acid, converting the potassium salt into the chloride, and heating the latter with water at  $150^\circ$ . It crystallises in slender transparent, deliquescent needles, and seems to be identical with Heinzelman's  $\beta$ -bromobenzenedisulphonic acid and Nöling's bromobenzenedisulphonic acid (see this Journal, 1878, Abst., 410, and vol. 13, 895, 1195, and Ber., 7, 1311). The normal salts dissolve readily in water; acid salts could not be obtained.

*Potassium bromobenzenedisulphonate*,  $\text{C}_6\text{H}_3\text{Br}(\text{SO}_3\text{K})_3 \cdot \text{H}_2\text{O}$ , obtained by decomposing the potassium diazo-salt with concentrated hydrobromic acid, crystallises in small white nodular masses.

The *barium* salt contains 4 mols.  $\text{H}_2\text{O}$ . The *silver* salt is anhydrous.

*Bromobenzenedisulphonic chloride*,  $\text{C}_6\text{H}_3\text{Br}(\text{SO}_2\text{Cl})_3$ , is formed by the action of phosphorus pentachloride on the potassium salt. It melts at  $103-105^\circ$ .

*Bromobenzenedisulphonamide*,  $\text{C}_6\text{H}_3\text{Br}(\text{SO}_2\text{NH}_2)_3$ , obtained by warming the chloride with strong ammonia, forms slender white needles (m. p.  $238^\circ$ ), sparingly soluble in cold, but readily in hot water.

*Action of Bromine on Paramidobenzenedisulphonic Acid*.—The products are tribromaniline, dibromamidobenzenesulphonic and paramidobromobenzenedisulphonic acids.

*Paramidobromobenzenedisulphonic acid*, [ $\text{SO}_3\text{H} : \text{SO}_3\text{H} : \text{NH}_2 : \text{Br} = 1 : 3 : 4 : 5$ ], consists of masses of slender microscopical needles, which have sometimes a silky lustre. It dissolves readily in water, and forms normal and acid salts, of which the former are the more soluble.

The *ammonium* salt,  $\text{C}_6\text{H}_3\text{Br}(\text{NH}_2)(\text{SO}_3\text{NH}_4)_3 \cdot 2\text{H}_2\text{O}$ , crystallises in transparent, bright yellow hexagonal prisms, which are decomposed with explosive violence by concentrated nitric acid.

The *potassium* salt resembles the ammonium salt; the normal salt of *barium* has 3, the acid 1, and the acid lead salt 5 mols. of  $\text{H}_2\text{O}$ .

The *diazobromobenzenedisulphonic acid*,  $\text{C}_6\text{H}_3\text{Br}(\text{SO}_3\text{H})\text{N}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained by the action of nitrous acid on bromoparamidobenzene-disulphonic acid in white tabular crystals, which are not explosive. They evolve nitrogen when their aqueous solution is heated. The *potassium* salt forms pointed microscopical prisms, and contains 3 mols.  $\text{H}_2\text{O}$ .

*Dibromamidobenzenedisulphonic acid* [ $\text{SO}_3 : \text{Br} : \text{NH}_2 : \text{Br} = 1 : 3 : 4 : 5$ ], crystallises in pale reddish crusts, formed of prisms containing  $2\text{H}_2\text{O}$ , which effloresce when exposed to the air. It is easily soluble in water, sparingly in spirit.

The *barium* salt with  $5\text{H}_2\text{O}$  forms white crystals, which acquire a red tint on exposure to air; they are slightly soluble, and are decomposed at  $180^\circ$ .

The *dibromide* of this acid yields a *dibromobenzenesulphonic acid*,  $[\text{SO}_3\text{H} : \text{Br} : \text{Br} = 1 : 3 : 5]$ , and also a tribromo-acid  $[\text{SO}_3 : \text{Br} : \text{Br} : \text{Br} = 1 : 3 : 4 : 5]$ .

(2.) *Orthamidobenzenedisulphonic acid* is obtained from orthamido-benzenesulphonic acid by the action of fuming sulphuric acid at  $170^\circ$ — $180^\circ$ , and is identical with disulphanilic acid. It crystallises in slender red microscopic needles, soluble in water, and forms normal and acid salts. Bromine precipitates tribromaniline (m. p.  $118.5^\circ$ ) from dilute aqueous solutions of the acid.

The *potassium*, *barium*, and *lead* salts have been prepared.

The *barium dibenzenedisulphonate* is obtained by the action of nitrous acid on a cold concentrated solution of the barium salt of the amido-acid.

(3.) *Metamidobenzenedisulphonic acid*,  $\text{C}_6\text{H}_5(\text{NH}_2)(\text{SO}_3\text{H}) \cdot 4\text{H}_2\text{O}$ , is formed from metamidobenzenesulphonic acid by heating it with fuming sulphuric acid at  $180^\circ$ . It forms rhombic octohedrons, easily soluble in water and in alcohol; it slowly absorbs moisture on exposure to the air, and quickly effloresces over sulphuric acid. When heated, it melts in its water of crystallisation and decomposes, leaving an easily combustible carbonaceous residue. Concentrated nitric acid causes it to deflagrate. It forms normal and acid salts, of which the latter are less soluble than the former. The salts of *ammonium*, *potassium*, *barium*, and *lead* have been prepared, and resemble in general characters the salts previously described. The acid potassium salt is anhydrous.

When metamidobenzenedisulphonic acid is acted on by nitrous acid a *diaz-acid* is formed, which yields salts with potassium, &c. When the *potassium* salt,  $\text{C}_6\text{H}_5(\text{KSO}_3) : \text{N}_2\text{SO}_3$ , is heated with alcohol under pressure, a new body is formed containing an acid, which the author names *oxethylbenzenedisulphonic acid*,  $\text{C}_6\text{H}_5(\text{EtO})(\text{SO}_3\text{H})_2$ . The *potassium* salt of this acid crystallises in slender, yellow transparent needles, soluble in water, and precipitated by alcohol from the aqueous solution as a white powder, redissolving in water with a yellow colour.

The *barium* salt crystallises with  $2\text{H}_2\text{O}$ , when the solution is rapidly evaporated, otherwise with  $3\text{H}_2\text{O}$ .

The *chloride*,  $\text{C}_6\text{H}_5(\text{EtO})(\text{SO}_2\text{Cl})_2$ , obtained from the acid by treatment with phosphorus pentachloride, forms white hexagonal plates (m. p.  $106^\circ$ — $105^\circ$ ), soluble in benzene, apparently forming a compound with it. Strong ammonia converts the chloride into the *amide*, which crystallises in nodular groups of needles (m. p.  $233^\circ$ ). This behaviour of the diazo-compound with alcohol is similar to that of orthamidotoluene-parasulphonic acid described by Hayduch (*Annalen*, 172, 215).

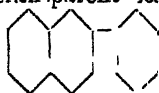
The *bromobenzenedisulphonic acid*,  $\text{C}_6\text{H}_5\text{Br}(\text{SO}_3\text{H})_2$ , is formed when hydrobromic acid acts on the diazobenzenedisulphonates (obtained from the acid metamidobenzenedisulphonates). It consists of slender, white deliquescent needles, and forms sparingly soluble normal salts, resembling in general characters those previously described.

*Bromobenzenedisulphonic chloride*,  $\text{C}_6\text{H}_5\text{Br}(\text{SO}_2\text{Cl})_2$ , melts at  $104^\circ$ .

*Bromobenzenedisulphonamide*,  $C_6H_5Br(SO_2NH_2)_2$ , formed by the action of ammonia on the chloride, forms slender silky needles (m. p.  $210^\circ$ ).  
G. T. A.

**Synthesis of Phenyl-naphthalene.** By W. SMITH (*Ber.*, 12, 2049—2053).—The author has recently shown that when a mixture of bromobenzene and naphthalene is passed through a red-hot tube containing pumice stone, phenyl-naphthalene,  $C_{11}H_7Ph$ , dinaphthyl, and diphenyl are formed. An increased yield of phenyl-naphthalene is effected by distilling the crude product, and again passing the first portion of the distillate mixed with a fresh portion of naphthalene through the red-hot tube.

The new hydrocarbon crystallises in colourless transparent scales (m. p.  $95^\circ$  corr.), and probably has the constitution



W. C. W.

**Action of Iodine on Oil of Turpentine.** By H. E. ARMSTRONG (*Ber.*, 12, 1756—1759).—When turpentine oil is heated in a retort with one-fourth its weight of iodine, no apparent change takes place until half the liquid has distilled over; at this stage hydriodic acid and iodine vapours are given off. The distillate is now poured back into the retort, and the distillation continued. These operations are repeated until iodine vapours are evolved as soon as the distillation is commenced; the product is then distilled in a current of steam. The residue consists of colophene; the chief portion of the distillate boils between  $155$ — $160^\circ$ ,  $175$ — $180^\circ$ , and at  $170^\circ$ ; it contains cymene and a mixture of two hydrocarbons of the composition  $C_{10}H_{20}$ , one of which boils at about  $160^\circ$ , and the other at about  $170^\circ$ . Cymene is the only hydrocarbon of the benzene series which is produced by this reaction.

W. C. W.

**Formation of Resin, and Chemistry of Ethereal Oils.** By DRAGENDORFF (*Arch. Pharm.* [3], 15, 50—54).—Of the two theories that have been proposed for the formation of resins, the author considers that the oxidation theory is the correct one. It was found that the oil of *Pinus pumilio*, when kept for a year in a flask, deposited a crystalline resin having the composition  $C_{20}H_{30}O_3$ ; it is hence inferred that all resins are produced by the oxidation of hydrocarbons. The presence of water does not appear to aid the formation of the resin. Certain oils after they have been kept for some time will no longer mix to a clear solution with excess of alcohol, although a small quantity of alcohol produces no turbidity. This turbidity is due to the precipitation of the resin which was dissolved in the oil.

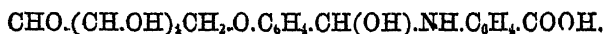
This theory is opposed to experiments made by Godeffroy and Liebermann (*Zeits. Oest. Apot.*, 15, 583), in which they found that oil freshly prepared from green juniper berries, became turbid on addition of alcohol. The author, however, found that oil of unripe juniper berries, prepared by himself, did not become turbid; he can, therefore, account for the results of Godeffroy only by the supposition that the oil from green junipers oxidises more rapidly than that prepared from the ripe berries.

E. W. P.



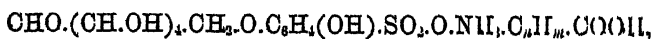
**Action of Zinc-dust on Resins.** By G. L. CIAMICIAN (*Gazzetta*, 9, 304—318).—The first two sections of this paper describing the products obtained from abietic acid and from elemi-resin, have already appeared in this Journal (Abst., 1878, 438, and 1879, 69). The third treats of the action of zinc-dust on gum ammoniac. The resin after being separated from the gum by means of alcohol is distilled with zinc-dust in a current of hydrogen, when it yields about 45 per cent. of an oily liquid. By distilling this in a current of steam, and by repeated fractional distillation, it may be separated into four portions—one boiling at 136—138°, which gives isophthalic and terephthalic acids on oxidation, and is a mixture of meta- and para-xylenes,  $C_8H_{10}$ ; the second (b. p. 160°) is *metamethylethylbenzene*,  $C_9H_{12}$ ; the third, boiling at 190—192°, the *methyl ether of orthoethylphenol*,  $C_8H_9MeO$ , which when heated with hydriodic acid yields methyl iodide and orthoethylphenol,  $C_8H_9O$ . The phenol is oxidised to salicylic acid by fusion with potash, and does not appear to be identical with any of the known ethylphenols (comp. *Annalen*, 102, 166; 156, 211 and 251; 170, 345). The fourth fraction (b. p. 235) is a homologue of benzene of the formula  $C_{13}H_{20}$ , and on oxidation with chromic mixture yields acetic and propionic acids and a small quantity of benzoic acid. C. E. G.

**Formation of Complex Glucosides.** By H. SCHIFF (*Ber.*, 12, 2032—2035).—Metamidobenzoic acid dissolves in a warm aqueous solution of helicin. On evaporating the liquid, a transparent, fluorescent, glass-like substance remains, which can be obtained in colourless plates (m. p. 142°) by recrystallisation from alcohol. This compound has the composition  $C_{13}H_{16}O_7 \cdot C_7H_7NO_2$ , or



By boiling with acids it is decomposed into glucose, an amido-acid, and an aldehydephenol. Similar crystalline compounds are formed when the hydrochlorides of amidocinnamic and amidosalicylic (1:2:5 and 1:2:5) acids are added to a solution of helicin in dilute soda. They are purified by recrystallisation from alcohol, and have the composition  $C_{13}H_{16}O_7 \cdot C_{10}H_{13}NO_2$  and  $C_{13}H_{16}O_7 \cdot C_7H_7NO_2$  respectively.

Unstable substances having the general formula



are obtained by dissolving helicin in an aqueous solution of amido-benzoic acid, glycocine, leucine, &c., saturating with sulphurous oxide, and evaporating the liquid over sulphuric acid.

These compounds slowly lose a portion of their sulphurous oxide at the ordinary temperature; they resemble the compounds of the aldehydes with acid potassium sulphite in their behaviour with dilute acids. W. G. W.

**Economical Process for Preparing Bibasic Quinine Citrate.** By F. DOTTO-SGRIBANI (*Gazzetta*, 9, 263—285).—Two processes are

at present employed for the preparation of quinine citrate, either by dissolving quinine in boiling water by the aid of citric acid, or by adding the requisite quantity of sodium citrate solution to quinine sulphate dissolved in 40 parts of boiling water. On cooling, quinine citrate crystallises out. The author finds it much more economical first to prepare calcium citrate by neutralising boiling lemon-juice with lime, washing the precipitate with boiling water, and, after drying, decomposing it with quinine sulphate. For this purpose 100 grams of quinine sulphate are dissolved in 3 litres of boiling water previously acidified with 3 669 grams sulphuric acid, 32·685 grams of the dry calcium citrate are added, and the whole boiled for half an hour. On cooling, the clear solution deposits quinine citrate in tufts of needles, which may be purified by recrystallisation. The mother-liquors yield a further quantity of the citrate on evaporation. C. E. G.

**Piperidine.** By R. SCHIFF (*Gazzetta*, 9, 333—335).—Considering the supposition that piperidine is a methylcrotonylamine as the most simple, the author determined to make attempts to reduce it, in hopes of obtaining normal methylbutylamine, but not succeeding, he then tried the reduction of a bromine derivative. He found that acetyl-piperidine in chloroform solution absorbed a molecule of bromine with avidity, but no crystalline compound could be obtained from it, neither did the action of reducing agents lead to any satisfactory result. He then prepared *phthalylpiperide*,  $C_6H_4(CO.NC_5H_{10})_2$ , by the evaporation of an alcoholic solution of piperidine (2 mols.) and phthalic anhydride (1 mol.). It forms large transparent crystals which readily unite with bromine, producing the compound  $C_6H_4(CO.NC_5H_{10})_2Br_2$ ; this crystallises in long colourless needles, very soluble in water or alcohol, but insoluble in ether. When treated with potash, it does not yield monobromopiperidine as might be expected, but all the bromine is removed, and the original compound is regenerated: silver oxide acts in a similar manner. From this it would seem improbable that the double bond in piperidine exists between two carbon atoms, but rather that it is between a carbon atom and a nitrogen atom. C. E. G.

**Alkaloids of "Alstonia Constricta."** By OBERLIN and SCHLAGDENHAUFFEN (*Pharm. J. Trans.* [3], 10, 1059—1060).—The bark was exhausted successively with ether, alcohol, and water, which took up 1·038, 27·740, and 1·375 per cent. respectively, but no examination was made of the alcoholic or aqueous extract. The orange-coloured residue left on evaporation of the ethereal extract was taken up with dilute hydrochloric acid (1 : 200), treated with animal charcoal, and precipitated with ammonia. The dried precipitate was then exhausted with ether, evaporated, taken up with dilute acid, and reprecipitated, repeating these operations until all colouring matter was removed. It was finally obtained in silky tufts of lustrous needles by recrystallisation from ether. It is soluble in ether, alcohol, chloroform, benzene, acetone, and light petrolum, moderately soluble in boiling water, but insoluble in the cold. It dissolves readily in dilute acids, and is precipitated by the same reagents as the other alkaloids. It is easily soluble in concentrated sulphuric, nitric, or hydrochloric acids, without

any perceptible coloration, but on diluting these solutions with water, a beautiful blue fluorescence is produced. Concentrated sulphuric acid and potassium dichromate colour the crystals of an intense blue-green, passing to violet and then to purple; on adding water a crimson solution is obtained.

The ethereal mother-liquors from which the alstonine had crystallised left an amorphous alkaloid on evaporation, which the authors propose to call *alstonicine*. It resembles alstonine in many points, but is only sparingly soluble in boiling water. It dissolves in concentrated sulphuric and hydrochloric acids with a greenish-brown tint; whilst with nitric acid it gives a splendid crimson-red. The acid solutions of the amorphous alkaloid do not exhibit fluorescence. The authors are of opinion that alstonine and alstonicine may possibly be related in the same way that quinine and quinicine are. C. E. G.

**Satureja Juliana.** By P. SPICA (*Gazzetta*, 9, 285—289).—This plant, called "*erva de ibbisi*" in the Sicilian dialect, is used by the peasantry to prepare a decoction which is taken in cases of intermittent fever: it is an herbaceous plant of the labiate order, having an aromatic odour, and somewhat pungent taste. In order to ascertain to what the active properties of the plant were due, the residue left on evaporating the alcoholic extract of the plant was washed with cold alcohol to free it as much as possible from chlorophyll, then dissolved in boiling alcohol, precipitated with an alcoholic solution of lead acetate, and filtered boiling. After separating the excess of lead by adding ammonia carbonate to the clear liquid, it was concentrated and precipitated with water. The substance was further purified by treating its alcoholic solution with animal charcoal and again precipitating with water. The white gelatinous product was separated by means of ether into two compounds, one of which, moderately soluble in ether (m. p.  $204-205^{\circ}$ ), gave numbers agreeing with the formula  $C_{14}H_{18}O_4$ , or, with less probability,  $C_{14}H_{16}O$ . The other substance, which is much less soluble in ether, especially in the cold, does not melt even at  $250^{\circ}$ , and above that temperature it is decomposed; the results of the analysis agree with the formula  $C_{14}H_{16}O_4$ . The more soluble substance acquires a greenish-yellow tinge when boiled with dilute sulphuric acid, but otherwise remains unchanged: a minute quantity dissolves, but the solution does not reduce Fehling's test, although when evaporated at  $100^{\circ}$  it blackens and emits an odour between that of wax and caramel. This is only a preliminary notice, the author intending to examine the plant more carefully as soon as he can obtain a sufficient quantity. C. E. G.

**Carica Papaya and Papayatin.** By J. PECKOLT (*Pharm. J. Trans.* [3], 10, 343—346, and 383—386).—The author gives a detailed description of the *Carica papaya*, or papaw tree, its growth and cultivation. The trees are dioecious and hermaphrodite; the hermaphrodite variety is called *Mamao macho* (male mamao), the fruit bearing variety *Mumao fema* (female mamao), and a cultivated variety of the latter *Mumao melao* (papaw-bearing mamao).

**Fruit.**—The fruit is gathered in the full-grown but unripe condi-

tion, when it contains a considerable quantity of a milky juice, which disappears almost entirely on ripening, and in the "mamao macho" is found a caoutchouc-like substance; in the "mamao femea," a soft yellow resin; and in the "mamao melao," a dark reddish-yellow fatty oil; these substances doubtless originated from the milky juice. The ripe fruit contained no free acid. The analyses of the fresh fruit of the three varieties freed from acid gave the following numbers:—

|                                     | Mamao femea. | Mamao melao. | Mamao macho. |
|-------------------------------------|--------------|--------------|--------------|
| Caoutchouc-like substance . . . . . | —            | —            | 0·046        |
| Soft yellow resin . . . . .         | 0 165        | —            | —            |
| Reddish-yellow fat . . . . .        | —            | 0·020        | —            |
| Albuminoids . . . . .               | 1·070        | 0·500        | 0·735        |
| Sugar . . . . .                     | 3·238        | 3·580        | 4·333        |
| Pectinous matter . . . . .          | 1·315        | 0·483        | 2·332        |
| Tartaric acid                       | 0·075        |              |              |
| Citric acid                         | 0·020        |              |              |
| Malic acid                          | 0·083        |              |              |
| Dextrin, &c. . . . .                | 5·503        |              |              |
| Water . . . . .                     | 85·351       | 92·500       | 89·445       |
| Cellulose . . . . .                 | 3·180        | 2·920        | 5·091        |

The fresh fruit of the "mamao femea" gave 1·239 per cent. of ash, and the dried fruit, 8·457 per cent. It contains a large amount of soda, potash, and phosphoric acid.

*Seeds.*—The examination of the seeds is not yet completed, but a detailed account of the method of analysis is given. They are found to contain:—An oil, *Papaya oil*; *Caricin*, an oil-like substance, with a disagreeable taste and smell, soluble in ether and alcohol; an acid similar to palmitic acid, *Carica fat acid*; a crystalline acid, *Papayic acid*, insoluble in cold water, but soluble in hot water and alcohol; a resin acid having an irritating and bitter taste, insoluble in water and ether, soluble in alcohol and alkalis; and a soft resin similar to that found in the fruit flesh of the "mamao femea."

*Milky Juice.*—This juice occurs in all parts of the plant, but in quantity only in the unripe fruit. It is extracted with difficulty, the method being to make longitudinal incisions through the skin of the growing fruit, and as soon as one wound ceases to yield any juice, another is made; the gathered fruit yields only a few drops of juice. The milk resembles sheep's milk, has a strongly acid reaction, and gelatinises when mixed with three times its volume of water; it is without smell, and its taste is astringent and bitter: its sp. gr. = 1·023 at 20°. Analyses of the milk were made in various ways.

(I.) The milk was repeatedly shaken with ether until nothing more was extracted. The ethereal solution, on evaporation, left a residue of wax, *Mamao wax*. The residue, insoluble in ether, was treated with alcohol, which extracted a resin, and the insoluble portion was treated with water and filtered; a caoutchouc-like substance remained on the filter; the filtrate was treated with absolute alcohol, when a white precipitate of *papayotin* was thrown down, which, when dried over cal-

cium chloride, formed an amorphous powder. The alcoholic filtrate contained a small quantity of extractive matter; 7.845 per cent. of papayotin was obtained by this method.

(II.) A quantity of the milk was evaporated to dryness, and the mass exhausted successively with ether, alcohol, and rectified spirit; the insoluble residue was dissolved in water, and alcohol added to the solution, when a light-brown precipitate separated out of *parapapayotin* (5.338 per cent.), a substance formed by the decomposition of papayotin by heat.

(III.) The milk was mixed with four times its volume of water, filtered from insoluble matter, and the filtrate treated with absolute alcohol. The precipitate was dried over calcium chloride, and consisted of snow-white papayotin to the amount of 3.762 per cent.

(IV.) The milk was exhausted repeatedly with warm water; the aqueous extracts concentrated, filtered, and precipitated with absolute alcohol; 4.304 per cent. of papayotin of a greyish colour was obtained.

(V.) The aqueous extracts of the milk were treated with lead acetate, the precipitates decomposed with sulphuretted hydrogen, and the filtered solution treated with absolute alcohol, in one case without and in another after concentration. A difference in the colour of the two products was all that was noticed.

*Milk from the Stem.*—The stem yields but a small quantity of milk, which had more the consistency of cream than that from the fruit. It contains 3.961 per cent. of snow-white papayotin.

*Green Leaves.*—The leaves yield 33 per cent. of a green juice, which is treated with absolute alcohol and filtered; the residue washed free from chlorophyll, and exhausted with water; the solution which contains impure papayotin is precipitated with basic lead acetate, and the precipitate treated as in No. V. A yield of .117 per cent. is obtained.

In the preparation of papayotin, strong heat should be avoided, to obtain an active product of a white colour. The best papayotin is obtained by method I or III, or from the stem; the most advantageous source, however, is the leaves, notwithstanding the small yield, since they can be obtained in large quantities. Papayotin is an amorphous, snow-white, non-hygroscopic powder, without smell, but with a slightly sweet, saline, astringent taste. It is insoluble in ether, alcohol, chloroform, and petroleum spirit, but soluble in glycerol and in water, nitric acid, and hydrochloric acid. Sulphuric acid colours it yellow; potash and soda colour it brown, and ammonia, yellow. An aqueous solution gave the following reactions:—White precipitates with alcohol, lead acetate, mercuric chloride, tannic acid, and sodium carbonate; with silver nitrate, a white turbidity, which, on standing, forms a deep yellow precipitate and a brown solution; iodine solution, a light-brown precipitate; ferric chloride, slight yellow precipitate; with phosphoric acid, on standing, a white precipitate; with Trommer's sugar-test, a beautiful violet-blue, which, after boiling, became red-violet.

Papayotin readily dissolves roasted meat; .28 gram dissolved .2 gram meat in 10 minutes. Parapapayotin has no action on cooked meat, even when heat is applied. Papayotin coagulates milk very

rapidly, as do those milk-juices of other Brazilian plants which have an acid reaction.

The fruit of the *Curica papaya* is used as a food, and the syrup formed by boiling the juice of the ripe fruit with sugar as a sedative and expectorant. The milky juice taken internally causes intestinal inflammation, but in small doses is given as a vermifuge, as are also the seeds. It is also used as a wash for the skin.

These results confirm those of Wittmack and Roy.

L. T. O'S.

**Lithofellic Acid and some Lithofellates.** By G. ROSTER (*Gazzetta*, 9, 364—393).—The finely-powdered oriental bezoar is extracted with boiling alcohol, and the filtered solution allowed to evaporate spontaneously, when it deposits the impure lithofellic acid in crystalline crusts. This, after recrystallisation, is converted into the sodium salt by neutralising the alcoholic solution with sodium carbonate, evaporating to dryness, and extracting the sodium lithofellate from the residue by treatment with boiling absolute alcohol. The sodium salt is converted into the corresponding barium salt by decomposing it in aqueous solution, with a slight excess of barium chloride, and may then be purified by recrystallisation.

*Barium lithofellate*,  $C_{20}H_{70}BaO_4 \cdot 10H_2O$ , may be obtained from its aqueous solution in very perfect prismatic crystals, as much as 4 cm. long; they have many lateral faces, and are terminated by rhombohedral summits. The measurements show that they do not differ much from the rhombohedric system. The crystals (m. p.  $185^\circ$ ) contain 10 mols. of water of crystallisation, of which they readily lose 4 in a dry atmosphere, and the remainder at  $150^\circ$ . The salt is very soluble in boiling water and in alcohol. Its rotatory power in aqueous solution, as determined with a Wild's polaristrobometer, is  $[\alpha]_D = +19.68^\circ$ , at a temperature of  $15^\circ$ .

*Lithofellic acid*,  $C_{20}H_{36}O_4 \cdot H_2O$ , is easily prepared from the barium salt by precipitating it in dilute solution with hydrochloric acid, and washing the precipitate with boiling water until the washings no longer give a precipitate with silver nitrate. Prepared in this way, it is a white crystalline powder (m. p.  $205^\circ$ , corr.), which may be obtained in distinct crystals from its alcoholic solution. The general appearance of these crystals is that of a hexagonal prism; but accurate measurements show that they are more complicated, and that they do not belong to the rhombohedric system, as stated by Hoppe-Seyler, but to the clinorhombic. The specific rotatory power of the acid in alcoholic solution is  $[\alpha]_D = +13.76^\circ$ , as determined with a Wild's polaristrobometer.

*Sodium lithofellate*, obtained by neutralising pure lithofellic acid with sodium carbonate and evaporating the aqueous solution, forms a gummy transparent mass, of pale yellow colour. It is exceedingly soluble both in water and in alcohol; its solutions have a very bitter taste. Its concentrated alcoholic solution, on cooling, deposits the sodium salt in microscopic crystals, consisting of stellate groups of slender needles. Its rotatory power at a temperature of  $14.5^\circ$  is  $[\alpha]_D = +18.16^\circ$ .

In recrystallising the crude precipitated barium lithofellate, a resi-

noid substance remains behind, apparently the barium salt of a new acid, but which the author has not as yet investigated.

The author considers that although lithofellic acid differs from the bile acids, and especially from cholalic acid in its crystalline form, in its behaviour with acids and with alkalis, and in its action on polarised light, it should yet be classed with them, considering the ratio of the carbon and hydrogen, its dextro-rotatory action, and its behaviour with Pettenkofer's reagent.

C. M. G.

**Diastase.** By M. BASWITZ (*Ber.*, 12, 1827—1831).—The author previously stated (*Ber.*, 11, 1443, and this Journal, 1878, Abstr. 903) that the presence of carbonic acid is favourable to the conversion of starch into sugar by diastase. He now finds that diastase acts on some specimens of commercial starch equally well in the absence of carbonic acid.

Potato-paste, rye meal, and barley extract contain a body which enables the diastase to convert the starch into sugar without the presence of carbonic acid.

The action of diastase on starch is not affected by increased or diminished pressure. The most favourable temperature is about 50°: above 60°, very little sugar is formed, the ferment being destroyed; whilst below 45° the formation of sugar takes place but slowly, although the maximum amount will be formed if the experiment is carried on for a sufficient length of time.

The quantity of sugar formed increases when the amount of diastase used is increased, but the increase is not proportional to the additional diastase.

W. C. W.

## Chemistry of Vegetable Physiology and Agriculture.

**Fermentation accompanied by formation of Hydrogen Sulphide.** By P. MIQUEL (*Bull. Soc. Chim.* [2], 32, 127—138).—A peculiar organism, existing in sewage water, has the power of converting not only combined, but even free sulphur into hydrogen sulphide. When placed in water containing solid albumin, this ferment causes the sulphur to be evolved in combination with hydrogen, until the amount of gas has increased to 60—70 c.c. per litre of liquid. The organism then dies. But if the solution be made alkaline with ammonia, soda, potash, or lime, about twice as much hydrogen sulphide is produced, before the ferment ceases to act. The sulphur contained in india-rubber is also evolved by this organism, and if the hydrogen sulphide be prevented from accumulating in the liquid, which can be accomplished by passing a current of carbonic anhydride through it, the evolution goes on as long as sulphur is present. A litre of water, to which had been added sulphur, 4 per cent. of normal urine, and a trace of the ferment, evolved 0.236 gram of sulphur combined with hydrogen in two days. To the naked eye, solutions undergoing this fermentation are almost limpid; the ferment, seen under the microscope,

forms elongated or circular cells of less than a thousandth of a millimeter in thickness. It is capable of existing in media free from oxygen.

W. R.

**Bacillus Ureæ.** By P. MIQUEL (*Bull. Soc. Chim.* [2], 32, 126—127).—This ferment, which exists in sewage, belongs to the class named *Anaerobies* by Pasteur; it resists exposure for some hours to a temperature of 95—96°, and causes urea to disappear from urino. It also removes urea rapidly from a solution of pure urea to which a little gelatin has been added.

W. R.

**Researches on the Bleeding of Vines.** By E. ROTONDI and A. GHIZZONI (*Bied. Centr.*, 1879, 527—530).—After giving the results of his analyses of the sap of vines cut in April and May, the first named author remarks that on the average a litre of vine-sap contains 0·147 gram of solids, and 0·052 gramm of ash, the red sorts yielding, however, more solids than the white; the time of cutting does not seem to have any influence on the quantity of phosphoric acid and potash contained in the sap. Ghizzoni's investigations lead him to the additional conclusion that sap taken from a lower part of the plant contains more mineral and less organic matter than that taken from upper parts.

J. K. C.

**Composition of the Kernels and Husks of the Seed of "Gleditschia Glabra."** By J. MOSER (*Bied. Centr.*, 1879, 388).—The author obtained the following results:—

|           | Water. | Protein. | Fat. | Non-nitrogenous extract. | Fibre. | Ash. | Sand. |
|-----------|--------|----------|------|--------------------------|--------|------|-------|
| Kernels.. | 10·90  | 20·94    | 2·96 | 51·68                    | 10·66  | 2·77 | 0·09  |
| Husks ..  | 1·24   | 4·54     | 3·67 | 60·70                    | 19·80  | 3·00 | 0·05  |

After boiling with dilute sulphuric acid, it was found that 41·4 per cent. of the kernels had been converted into dextrose.

Tannic acid was found to be present in the husks to the extent of 7·7 per cent.

J. K. C.

**Ash of Different Parts of the Vine.** By E. ROTONDI (*Bied. Centr.*, 1879, 530—532).—The following briefly noticed investigations of the mineral constituents of the must, branches, and leaves of the vine relate to the products of two vine hills in the neighbourhood of Asti, on each of which were planted three kinds. The author gives the results of his analyses in tabular form, and infers from them that the composition of the ash varies with the locality rather than with the sort of vine; potash is found in greatest quantity in the ash of the must (60 to 70 per cent.), and in the least (6 per cent.) in that of the leaves, the latter also being poorest in phosphoric acid, and very rich in lime and silica. Soda is absent in all the samples analysed.

J. K. C.

**Agricultural Chemistry in Japan.** By E. KINCH (*Chem. News*, 40, 195, 196).—This is a short account of the collection of soils,



manures, and agricultural products, shown by the Imperial College of Agriculture, Japan, at the International Exhibition, at Sydney. Accompanying the collection is a report containing analyses of the greater number of the products, from which Mr. R. Warington has selected those of the principal foods, such as rice, soy beans, sweet potato, large radish, sea-weeds, tea, and saki. The last, a fermented liquor prepared from rice (this Journal, 1879, Abst., 413), contains from 11.33 to 15.0 per cent. of alcohol, and the free acid, reckoned as acetic acid, amounts to 0.20 to 0.27 per cent. Besides these, the report contains analyses of manures, including lime, wood-ashes, nitre, waste vegetable substances, and residue from various manufactures, fish manure, bone superphosphates, excrement of birds, and hair. There is also a summary of the principal dye-stuffs and their methods of preparation, and the analyses of the most important. The different oils and waxes form the concluding section of the catalogue.

L. T. O'S.

**Method of Selecting Beet for Seeding.** By D. BLEED (*Bied. Centr.*, 1879, 535—536).—This is usually done by taking the specific gravity of the whole root; but on account of the difficulties connected with this plan, the author suggests that pieces be cut out of the root, about one third from the top; these do not differ greatly in specific gravity from the rest of the root, and should be placed in a bath of salt of 105°, only those roots the cuttings from which sink being used for seed.

J. K. C.

**Relation of the Colour of Clover Seed to its Value.** By G. HABERLANDT (*Bied. Centr.*, 1879, 532—534).—The author divides clover seed into two groups, the one comprising the yellow and violet being more valuable and less altered by keeping than the other group, in which he includes the brown and gray seeds.

J. K. C.

**Absorptive Power of Soil-constituents for Gases.** By G. AMMON (*Bied. Centr.*, 1879, 511—515).—The substances used in these experiments were sand, aluminium silicate, calcium carbonate, hydrated oxide of iron, gypsum, clay, and humus, all powdered to various degrees of fineness. The author tried the effect of aqueous vapour and ammonia on these substances at various temperatures; his experiments showing that the most favourable temperature for absorption lay between 0° and 10°, and that the quantity absorbed varied directly with the fineness to which the substance had been powdered. The following are the numbers obtained, 100 c.c. of each substance being used, and the water being calculated by volume in the state of gas:—

Cubic centimetres of water-vapour condensed by

| At      | Humus. | Hydrated iron oxide. | Quartz. | Calcium carbonate. | Kaolin. |
|---------|--------|----------------------|---------|--------------------|---------|
| —10° C. | 12717  | 12973                | 2026    | 208                | 5378    |
| 0       | 14206  | 47332                | 2198    | 4258               | 5375    |
| 10      | 36504  | 99712                | 1185    | 4775               | 6447    |
| 20      | 26789  | 98990                | 277     | 962                | 1541    |
| 30      | 16497  | 54753                | 99      | 233                | 1335    |

Of ammonia gas at 0° C. the following quantities were absorbed:—

| By humus. | By hydrated<br>iron oxide. | By quartz. | By carbonate<br>of lime. | By kaolin. |
|-----------|----------------------------|------------|--------------------------|------------|
| 29517     | 38992                      | 938        | 1552                     | 2417       |

Part of the ammonia was converted into nitric acid by the oxide of iron. Carbonic anhydride was absorbed in very small quantity, except in the case of hydrated oxide of iron, from which the gas could not be expelled by air, as was the case in the other materials employed.

By treating the soil-constituents with marsh-gas, empyreumatic substances were formed which prevented the experiments in this direction being completed. The condensation was greatest in the case of hydrated oxide of iron. Treatment with sulphuretted hydrogen was followed by a separation of sulphur in the case of all the substances employed: the greatest increase in weight was observed in gypsum. Oxygen was not absorbed by quartz, carbonate of lime, or kaolin: humus even lost in weight by exposure to the gas; 100 c.c. of gypsum absorbed 1189, and 100 c.c. hydrated oxide of iron absorbed 665 c.c. of oxygen. The condensation power for nitrogen was greater, as is shown by the following numbers:—

| 100 c.c. of                      |        |                         |       |                       |         |         |
|----------------------------------|--------|-------------------------|-------|-----------------------|---------|---------|
|                                  | Humus. | Hydrated<br>iron oxide. | Sand. | Carbonate<br>of lime. | Kaolin. | Gypsum. |
| Absorbed c.c. }<br>of nitrogen } | 126    | 23986                   | 24    | 3803                  | 813     | 10253   |

In this case also nitric acid was found in the aqueous extract from the hydrated oxide of iron.

To show the influence of oxide of iron on the absorption of nitrogen by the soil, the author made the following determinations, in which ferruginous sand and clay, and the same substances freed from iron by hydrochloric acid, are compared in their absorptive power for nitrogen:—

| 100 c.c. of sand |     |       |  | 100 c.c. of kaolin |                       |
|------------------|-----|-------|--|--------------------|-----------------------|
| Containing iron. |     | Pure. |  | Containing iron.   | Pure.                 |
| Absorbed. .      | 217 | 101   |  | 1687               | 816 c.c. of nitrogen. |

J. K. C.

**Experiments on the Manuring of Barley.** By P. WAGNER and W. ROHN (*Bied. Centr.*, 1879, 515—519).—The soil in which these experiments were carried out was a sand containing 1½ per cent. of humus, the phosphate being applied in the following experiments one day before, and the nitrogen (in the form of Chili saltpetre) the day after sowing. The following table shows the quantities of manure applied per hectare and the yield obtained:—

|   | Corn.<br>Kilos. | Straw.<br>Kilos. |
|---|-----------------|------------------|
| (1.) Unmanured.....                         | 4420            | 3770             |
| (2.) 20 kilos. nitrogen .....               | 5280            | 4890             |
| (3.) 50 kilos. soluble phosphoric acid..... | 4570            | 4400             |

|  | Corn.<br>Kilos. | Straw.<br>Kilos. |
|--|-----------------|------------------|
| (4) 50 kilos. soluble phosphoric acid with 20 kilos. nitrogen.....   | 5320            | 4920             |
| (5.) 50 kilos. phosphoric acid in the form of freshly precipitated calcium phosphate, and 20 kilos. nitrogen .....     | 5600            | 5110             |
| (6.) 50 kilos. soluble, with 43 kilos. insoluble phosphoric acid in form of phosphorite, with 20 kilos. nitrogen ..... | 5970            | 5370             |
| (7.) 35 kilos. soluble, and 30 kilos. insoluble phosphoric acid as above, with 20 kilos. of nitrogen .....             | 5660            | 5350             |
| (8.) 50 kilos. soluble phosphoric acid in the form of phosphate of potash, with 20 kilos. nitrogen.....                | 6170            | 6500             |

It is evident from the above that although the soluble phosphoric acid yielded poor results, the use of saltpetre proved very advantageous. The reason of this may be looked for in the fact that the soil was so very poor in lime as not to be able to arrest the phosphoric acid during its percolation through the soil after rains, thus only a small quantity of it came into actual contact with the roots of the barley. This was of course different in the cases of experiments (5), (6), and (7), where part at least of the phosphoric acid was applied in the insoluble form, and larger yields were the result. With regard to experiment (8), the authors do not explain whether the remarkable yield obtained was the result of the way in which the phosphoric acid was combined, or of the presence of potash.

J. K. C.

**Manuring Experiments with Oats.** By C. JENSEN (*Bied. Centr.*, 1879, 519—523).—A field was marked off into eleven plots of 975 square metres each; of these two were not manured, the remaining nine being treated with quantities of manure of various sorts equal in value commercially. The table following shows the various manures used and the resulting produce:—

|                               | Quantity<br>applied<br>per hectare.<br>Kilos. | Yield in         |                  |                  |
|-------------------------------|---|------------------|------------------|------------------|
|                               |   | Grain.<br>Kilos. | Straw.<br>Kilos. | Chaff.<br>Kilos. |
| Chili saltpetre .....         | 19  | 201              | 268              | 29               |
| Unmanured .....               | —   | 151              | 190              | 18               |
| Bone meal .....               | 25  | 181              | 227              | 21               |
| Bone meal superphosphate....  | 25  | 173              | 216              | 21               |
| Ammoniacal superphosphate ..  | 22  | 177              | 199              | 20               |
| Peru guano .....              | 16  | 181              | 209              | 17               |
| Unmanured .....               | —   | 168              | 194              | 16               |
| Bone guano superphosphate ..  | 31  | 194              | 242              | 17               |
| Animal manure.....            | 17.5  | 172              | 213              | 18               |
| Stable dung .....             | 1100  | 194              | 233              | 23               |
| Mejillon guano superphosphate | 29.5  | 170              | 200              | 14               |

The above tables show that Chili saltpetre, and next to it stable dung and bone guano superphosphate, produced the best yields. Further researches are necessary to establish any conclusions from the above results. J. K. C.

**Manuring of Beetroot.** By O. VIBRANS (*Bied. Centr.*, 1879, 525).—The object of these investigations was to ascertain the value of the potash contained in molasses lees and charcoal residues as a manure. The action of several other well-known manures was tried, with results not differing much from the ordinary. From his experiments the author draws the conclusion that the potash of the charcoal residues is in a form which can be more readily absorbed by the beet than the potash of the lees. J. K. C.

**Manuring of Beetroot.** By H. BODENBENDER (*Bied. Centr.*, 1879, 523—524).—Samples of the sugar-beet taken from plots of land to which various manures had been applied, were tested for sugar at different periods of their growth. The seeds were sown on the 9th of May, and from the 1st of August to the 14th of September the plants were subjected to quantitative investigation. On the results of his researches the author makes the following remarks:—Nitrogen when applied as manure in the form of Chili saltpetre, delays the ripening of the root to a considerable extent, and lessens the percentage of sugar, although the yield by weight of the root is much increased. Phosphoric acid and guano give very favourable results as regards the percentage of sugar in the yield. J. K. C.

## Analytical Chemistry.

**Apparatus for Estimating Oxygen in the Atmosphere.** By F. FISCHER (*Ber.*, 12, 1696—1698).—The oxygen in the atmosphere is determined by measuring the diminution in volume which takes place when a copper spiral is heated to redness, by means of a galvanic current in a known volume of air. A description of the apparatus and full details of the process employed are given in the original paper. W. C. W.

**Quantitative Estimation of Oxygen dissolved in Water.** By F. TIEMANN and C. PERUSSE (*Ber.*, 12, 1768—1789).—The authors have examined three methods of determining the amount of oxygen dissolved in water, viz.:—

1. Mohr's volumetric process (*Mohr's titrimethode*) in which soda and a standard solution of ferrous sulphate are added to 500 c.c. of the water, which must be heated to 40°; after an interval of half an hour the precipitated ferrous hydroxide is dissolved in sulphuric acid, and the unoxidised ferrous salt determined by titration with potassium per-

manganate. From the amount of ferrous sulphate oxidised by the water, the quantity of oxygen is easily calculated. The results obtained by this method are invariably too low.

2. *Gasometric Method*.—In order to expel the dissolved gases from the water, a slightly modified form of Reichardt's apparatus (*Zeits. Anal. Chem.*, 11, 271, and this Journal, 26, 412) is employed. In presence of combustible gases, e.g., marsh-gas, the oxygen is determined by absorption with potassium pyrogallol, but when the mixture contains only oxygen, nitrogen, and carbonic anhydride, the latter is removed by a solution of soda, and the oxygen estimated by explosion with hydrogen. This method yields excellent results, but requires complicated apparatus. In certain cases when the water is boiled to expel the gases, there is a risk of a part of the oxygen not being evolved, owing to its having oxidised some of the constituents of the water.

3. The process of Schützenberger and Risler (*Bull. Soc. Chim.*, 19, 153, and 20, 145) is very accurate, and seems to be the best adapted for general use. In this method, the oxygen is determined by the amount of indigo-white it converts into indigo-blue. Standard solutions of ammoniacal copper sulphate, sodium hyposulphite,  $\text{Na}_2\text{SO}_3$ , and indigo-carmin are required.

The standard copper solution is prepared by dissolving 4.469 grams of  $\text{CuSO}_4 + 5\text{H}_2\text{O}$  in water, adding excess of ammonia, and diluting to a litre with water free from air; 10 c.c. of this solution are equivalent to 0.0014386 gram, or 1 c.c. oxygen at  $0^\circ$  and 760 mm. The hyposulphite solution is prepared by treating with zinc-dust for five minutes a solution of commercial sodium hydrogen sulphite, which has been diluted to sp. gr. 1.25. The liquid is now mixed with ten times its volume of boiled water, separated from the zinc-dust by decantation, and transferred to stoppered bottles, milk of lime being added until a slightly alkaline reaction is produced. The precipitated zinc oxide is allowed to settle, and the supernatant liquid is rapidly filtered. To standardise the hyposulphite, 10 or 25 c.c. of the standard ammoniacal copper solution are brought into a Woulf's flask, from which the air is displaced by a current of pure hydrogen. The hyposulphite is added from a burette, the point of which passes through a cork in the tubulus of the Woulf's bottle. The exact point when the blue copper solution is completely decolorised by the hyposulphite is easily observed. After this experiment, the hyposulphite is diluted with water free from air until 5 c.c. are required to reduce 10 c.c. of the copper solution.

The indigo solution is prepared by dissolving 100 grams of commercial indigo carmine paste or commercial indigotin (sodium indigo sulphate) in 2 litres of water. Its strength, which should equal that of the ammoniacal copper solution, is determined by titration with hyposulphite.

The apparatus required for the determination consists of a three-necked Woulf's bottle, of  $1\frac{1}{2}$  litres capacity, which stands in an evaporating basin, containing warm water. Each tubulus is provided with a double-bored cork; through the first pass a thermometer and a glass tube, connected with an apparatus for generating pure hydrogen. The

second contains two drawn out pieces of glass tubing, which are attached by means of a caoutchouc tubing to the burettes containing the standard hyposulphite and indigo solutions. The upper end of the hyposulphite burette is provided with a tube containing pumice stone soaked in potassium pyrogallate. A funnel fitted with a stop-cock, and a glass tube bent twice at right angles, and dipping into water, pass through the cork in the third tubulus.

About 250 c.c. of warm water free from air, and 30—40 c.c. of the indigo solution, are brought into the flask, from which the air is expelled by a current of hydrogen. The contents of the flask must be kept at a temperature of 45° during the experiment. Standard hyposulphite is added until the indigo is bleached. 250 c.c. of the water to be examined are now brought into the flask through the tap funnel, care being taken to prevent the admission of air. The mixture is well shaken, and hyposulphite added until the blue colour is destroyed. From the c.c. of hyposulphite used, the quantity of oxygen may at once be calculated, e.g., 4.2 c.c. hyposulphite are equivalent to 10 c.c. of the standard copper solution = 0.0014336 gram, or 1 c.c. oxygen. 250 c.c. water required 7.2 c.c. hyposulphite, or 28.8 per litre,  $\frac{28.8}{4.2} =$

6.85 c.c. of oxygen at 0° and 760 mm. Three oxygen determinations in succession may be made without changing the apparatus; but since the hyposulphite changes rapidly, its strength must be determined by titration with ammoniacal copper solution every time the burette is filled.

W. C. W.

**Water Analysis.** By A. MÜLLER (*Arch. Pharm.* [3], 15, 25—27).—The residue obtained by evaporating the water is usually heated to 120—140°. This temperature is insufficient to remove the crystalline water of magnesium and calcium sulphates, therefore the solid matter is always reported too high. It is advisable therefore always to add a known weight of sodium carbonate, and subsequently to neutralise after separation of the earths according to the process described in *Ber.*, 1870.

E. W. P.

**Estimation of Sulphur in Natural Sulphides.** By A. COLSON (*Bull. Soc. Chim.* [2], 32, 115—116).—The method described is particularly applicable to estimation of sulphur in pyrites. The sample is placed in a platinum boat near the sealed end of a piece of combustion tube, the other end of which is closed with a double-bored india-rubber cork. Through one of the holes a tube passes to the end of the combustion tube, and conveys oxygen to the sulphide, whilst the resulting sulphurous anhydride escapes through the other tube into soda. The sulphurous acid may be estimated by the iodine process, and the sulphuric acid by baryta, or if a standard solution of soda be used, the portion remaining unneutralised may be estimated with standard acid, and the total sulphur deduced by calculation.

W. R.

**Testing for Nitric Acid in Presence of Nitrous Acid.** By A. PICCINI (*Gazzetta*, 9, 395—396).—This method is useful for detecting

minute quantities of nitrates in the presence of large quantities of nitrites, and is founded on the property urea has of decomposing the latter in acid solution. Urea is added to the solution containing the nitrate, and it is then gradually added to another solution of urea in dilute sulphuric acid. As soon as the evolution of nitrogen due to the decomposition of the nitrites has ceased, some iodised starch is added, and then a fragment of zinc, when a blue coloration is produced if any nitrate is present. C. E. G.

**Analysis of Superphosphates.** By E. WEIN, L. RÖSCH, and J. LEHMANN (*Annalen*, 198, 290—307).—As adverse criticisms have been made against the process which was adopted at the Magdeburg Conference in 1872 for the extraction of soluble phosphoric acid from superphosphates, the authors have investigated the different points objected to, and some of the methods which have been proposed to be substituted for it. In their opinion the differences which frequently arise in the analysis of superphosphates are to be attributed entirely to a want of uniformity in preparing the aqueous solution, and not to the method that may be employed for the determination of the soluble phosphoric acid. The points investigated were as follows:—

a. *The time necessary for Digestion.*—In the opinion of Abesser, Jani, and Märcker (*Zeits. Anal. Chem.* 12, 239), a digestion of the superphosphate in water for a few minutes is sufficient, as by digestion for a longer time more soluble phosphoric acid may be obtained than was originally present as such, probably owing to the action of free sulphuric acid on the phosphate.

On the other hand, too low results are possible either from a transformation of soluble monocalcium phosphate into insoluble dicalcium phosphate, or, in the presence of oxides of iron and alumina from the formation of insoluble phosphates of these bases.

With these statements the authors entirely disagree. Their experiments prove that although in some cases a shorter time may suffice, yet with all kinds of superphosphates, whether containing much or little iron oxide and alumina, a digestion in cold water for two hours gives the most accurate results.

b. *The Extraction of the Soluble Phosphoric Acid by Washing the Superphosphate on a Filter which is connected with a Bunsen's Pump.*—This method has been recommended by Fresenius, Luck, and Neubauer (*Zeits. Anal. Chem.*, 7, 304); and by Märcker, who states that the reduction of the soluble phosphoric acid is thereby avoided. The authors, however, obtained results from nine different kinds of superphosphates which were from '06 to '825 p. c. too low, arising no doubt, as explained by Erlenmeyer, from the decomposition on the filter of the monocalcium phosphate owing to the absence of free phosphoric acid. In the presence of excess of free phosphoric acid, this process was accurate, and this is believed to explain Fresenius's results, which were obtained with a superphosphate containing 5.85 p. c. free phosphoric acid.

c. *The quantity of Water which is necessary for Complete Extraction.*—With the exception of a slight increase in the amount of soluble phosphoric acid from superphosphates containing much oxide of iron

and alumina, no advantage is gained by increasing the quantity of water above that used in the Magdeburg process.

The authors' results, therefore, confirm the accuracy of the Magdeburg method, which consists in digesting 20 grams of the superphosphate in a litre of cold water for two hours.

A. J. C.

**Superphosphates from Pure Tricalcium Phosphate.** By E. WEIN (*Annalen*, 198, 307—318).—In order to ascertain the cause of the difference in the results obtained by the methods described in the previous paper, similar experiments were made with calcium superphosphates which had been prepared by the action of sulphuric acid on pure tricalcium phosphate in such a manner as to obtain superphosphates of three kinds, *a*, *b*, *c*.

The soluble phosphoric acid was in all cases determined by the molybdic acid method. The results are as follows:—

*a. Superphosphates which contain much Free Phosphoric Acid* (11.35 p. c.).—A very short period of digestion in water is sufficient to extract the whole of the soluble phosphoric acid. An increase in the quantity of water (1000 c.c. for 20 grams) is unnecessary. Correct results are obtained by washing the superphosphate on a filter-pump, but the quantity of wash water required before the filtrate is free from acid, that is, before the extraction is completed, is considerably greater than 125 c.c. for five grams, as stated by Märcker.

*b. Superphosphates containing only a Small Quantity of Free Phosphoric Acid* (0.5 p. c.).—It is necessary to continue the digestion in water for two hours to be certain that the extraction is completed. Washing on a filter-pump gives results which are considerably too low for the reasons stated in the previous paper.

*c. Superphosphates with no Free Phosphoric Acid.*—Digestion in water for two hours is also necessary in this case: the filter-pump method is wholly inapplicable.

If superphosphates, which contain mono- and di-calcium phosphates but no free acid, are treated with more than the usual quantity of water, *e.g.*, with 5 : 1000, then more soluble phosphoric acid is obtained than when the same superphosphate is digested for two hours in the way recommended, that is 20 : 1000. This result is due to the solubility of the di-calcium phosphate. The opposite results obtained by Wattenborg (*J. für Landwirthsch.*, 1879, 27—52) on this point are stated to be due in all probability to the presence of free phosphoric acid which the author found could only be removed with great difficulty from a mixture of mono- and di-calcium phosphates.

The decomposition of monocalcium phosphate which occurs according to Erlenneyer (*Ber.*, 9, 1839) when it is treated with a small quantity of water is too trifling to affect the results.

The conclusions therefore arrived at in the previous paper are confirmed.

A. J. C.

**Estimation and Separation of Manganese.** By J. VOLHARD (*Annalen*, 198, 318—364).—The volumetric method proposed by Guyard (*Bull. Soc. Chim.* [2], 1, 88) for the determination of manganese in a manganous salt by titrating the neutral and very dilute solution with a standard solution of potassium permanganate, has not



been found to give exact results on account of the precipitate which is caused by the permanganate being always of an uncertain and variable composition, and because of the extreme difficulty in ascertaining the end of the reaction. Guyard stated that the whole of the manganese was precipitated as  $\text{MnO}_2 \cdot \text{Mn}_2\text{O}_7$ .

The author shows that if a salt of calcium, magnesium, barium or zinc, be added to a solution of manganous salt, the whole of the manganese is precipitated by potassium permanganate as dioxide;\* moreover, the end of the reaction can be very readily observed, as the precipitate settles rapidly and the supernatant liquid becomes quite clear. The reaction occurs according to the equation,  $3\text{MnO} + \text{Mn}_2\text{O}_7 = 5\text{MnO}_2$ .

The salts of all strongly basic metallic oxides which are not susceptible of oxidation, have a similar action. Alkaline salts to a great extent obscure the end of the reaction.

Prefatory to describing the modified process, the author's opinions are expressed on several points more or less connected with it.

*Titration of the Solution of Potassium Permanganate.*—Objections are made against most of the usually adopted methods for standardising this solution. The use of the double salt of iron and ammonium is specially objected to on account of the difficulty of obtaining it free from ferric salt.

Methods are described by which it can be standardised by determining the manganese in it, either as sulphate or as oxide,  $\text{Mn}_2\text{O}_3$ . In either case the permanganate is reduced by sulphurous or hydrochloric acid, and the manganese after precipitation by ammonium carbonate is converted into sulphate, or into oxide by igniting the chloride with mercuric oxide.

The mercuric oxide used for this purpose is prepared by precipitation (with pure sodium hydrate) from the chloride which has been sublimed from a mixture of the chloride with one-tenth its weight of oxide; thus prepared, it can be similarly employed with great advantage for the conversion of most metallic chlorides into oxides; and to precipitate ferric or aluminic oxide, when in solution as chloride, free from alkalis, but not from alkaline earths; also to separate ferric oxide completely from manganese.

To any of the methods above mentioned, the author prefers to standardise the permanganate solution by means of a solution of potassium iodide in presence of hydrochloric acid, determining the liberated iodine in the usual way with standard sodium thiosulphate and calculating the manganese from 80 mgrms.  $\text{O} = 3 \times 55 = 165$  mgrms. Mn. The solution of permanganate must be free from chlorates, and the water used in the process from nitrites. The solutions required are potassium permanganate containing 3.833 grams per litre, 1 c.c. = 2 mgrms. Mn; sodium thiosulphate prepared by dissolving 30.061 grams with addition of 3 grams of ammonium carbonate in 1 litre of water, 1 c.c. = 2 mgrms. Mn, and a solution of potassium iodide approximately equivalent to 55 grams free hydriodic acid per litre.

\* Kessler has previously used zinc chloride for the same purpose in precipitating a manganous salt with bromine (*Zeits. Anal. Chem.*, 1879, I—II, and this Journal, 1879, 341, Abst.). Pattinson subsequently found that ferric chloride had a similar action (this Journal, 1879, 365, Trans.).—A. J. C.

*Separation of Iron from Manganese.*—Iron is the only metal which, if present in large quantity, hinders the determination of manganese by this method. In preference to any other method, the author separates the iron from manganese by precipitation with zinc oxide, which can be prepared for this purpose by igniting ordinary zinc white and levigating it with water.

In the absence of iron or in the presence of a small quantity of it, the process is as follows:—

The solution of manganous salt is mixed with about 1 gram of zinc sulphate and diluted so that 100 c.c. does not contain more than 0.25 gram Mn, and if the solution is neutral 2 to 3 drops of nitric acid (1.2 sp. gr.) are added; if acid, it is neutralised with sodium carbonate (free from sulphite) and nitric acid then added as before. The solution is heated to boiling, and the solution of permanganate added until the colour remains permanent. Properly performed, the titration occupies from twelve to fifteen minutes. A blank experiment must be made with the solution of zinc sulphate.

Metallic alloys, wrought iron, and steel, are dissolved in a mixture of 3 vols. of sulphuric acid (1.13 sp. gr.) and 1 vol. of nitric acid (1.4 sp. gr.). Substances dissolved in hydrochloric acid are evaporated to dryness with sulphuric acid, and then taken up with water. Spiegelleisen or ferromanganese is dissolved in nitric acid, the solution then evaporated to dryness, and the residue heated until the nitrate is decomposed and carbonaceous matter is burnt off. The residue is dissolved in hydrochloric acid, and this acid expelled with sulphuric acid as before described. In all cases, the greater part of the acid is neutralised with sodium carbonate or sodium hydrate (free from manganese), then zinc oxide is added until the supernatant liquid is milky, showing that the whole of the iron has been precipitated.

The oxide of iron precipitate generally settles so rapidly that it is unnecessary to filter, and a portion of the liquid can be taken off with a pipette and the manganese determined as before.

*Separation of Manganese from other Metals in a Strongly Acid Solution.*—Manganese is usually separated from other metals by precipitation in a slightly acid or neutral solution by means of lead dioxide, chlorine, or bromine. It has been found possible to do this in a strongly nitric acid solution, with lead oxide as a precipitant, in a manner which is described by the author; but the method is not recommended, and the following is considered preferable:—The solution of manganous compound is heated to boiling with strong nitric acid and pure mercuric oxide. Chlorine or bromine water is added until the oxidation is completed, which is shown either by the solution being red or becoming quite clear. In this manner, from a solution containing 0.5 gram pure manganous sulphate and 15–20 c.c. nitric acid (1.2 sp. gr.), and about 1 gram mercuric oxide, the manganese is completely precipitated in 15–20 minutes. The precipitate is then heated to redness to expel mercuric oxide, and can be weighed either as oxide or as sulphate. If cobalt, nickel, zinc, calcium, magnesium or potassium are present, the precipitate should be dissolved and reprecipitated.

*Precipitation of Manganese by Oxidising Agents.*—The author dis-

cusses the formation of the precipitate which is produced when an oxidising agent is added to a solution of manganous salt, and he expresses the opinion that permanganic acid is most probably the first result of the oxidation, and this combines with the manganous oxide, so that the whole of the manganese is precipitated as dioxide ("hyperoxide").\* In furtherance of this view, it is shown that either permanganic acid or dioxide can be obtained as the result of the oxidation; in fact, Crum's test for manganese depends on producing the one, viz., permanganic acid, in presence of nitric acid, leaving no manganous oxide in solution, in which case the solution retains the colour of permanganic acid.

Crum's test is best performed by heating almost to boiling 10 c.c. of a solution made from equal parts of nitric acid (sp. gr. 1.2) and water containing a little plumbic dioxide, then adding the dilute solution of manganese compound; the coloration occurs immediately even in presence of chlorides. It has been proposed to use Crum's test for the quantitative determination of manganese, but it cannot be used when the amount of manganese in solution exceeds 100 mgrms., as this appears to be the maximum that can be oxidised to permanganic acid without precipitation of oxide.

Titration with potassium permanganate as above described is considered to be quite as delicate for the detection of minute quantities of manganese.

A. J. C.

**Experiments with Scheibler's Method of Analysing Raw Sugar.** By H. WICHELHAUS, K. FISSMELD, and K. STAMMER (*Biel. Centr.*, 1879, 542).—Scheibler's method consists in boiling the raw sugar with a saturated alcoholic solution of sugar, and weighing the residue. After numerous experiments with various kinds of raw sugar, it was found that on the average Scheibler's method gave fairly good results, no variation being greater than one and a half per cent.

J. K. C.

**Estimation of Sugar in Beet Juice.** By C. BITTMAN (*Arch. Pharm.* [3], 15, 63—69).—In the manufacture of sugar from sugar-beet, there always appears to be a loss of sugar during the filtering and concentration of the juice. This loss is, however, only apparent, as the amount of sugar is estimated by the polariscope, and is consequently affected by the presence in the raw juice of dextrin, ambic acid, and asparagin; these being dextrorotatory cause the amount of sugar to appear greater than it really is. The total amount of sugar in the roots is sometimes deduced from the amount of sugar in the juice as follows:—If the sugar in the juice amounts to say 12 per cent. and the mark 5 per cent. of the roots, then the percentage of juice is 95 per cent., and the percentage of sugar in the roots is  $12 \times 0.95 = 11.4$ . This calculation takes for granted that the amount of sugar in the whole of the juice coincides with that found in the sample, that is, that the cells of the root contain a homogeneous liquid. This hypothesis the

\* Wright and Luff (this Journal, 1878, 513) have shown that the precipitate produced on adding bromine to manganous chloride containing excess of caustic soda, consists of dioxide mixed with a certain amount of lower oxide. - A. J. C.

author combats, and quotes in corroboration Yicinsky, Heintz, and Scheibler, who state that every portion of the juice in the root must not be considered as holding equal quantities of sugar in solution that in the root there is water containing no sugar, and which must be considered as water of organisation. The conclusion drawn is, that the present method of determining the amount of sugar in sugar-beet is very unsatisfactory. E. W. P.

## Technical Chemistry.

**Burning of Fuel in House Stoves.** By F. FISCHER (*Dingl. polyt. J.*, 233, 133—136).—During the 18 months previous to January, 1879, 56 patents for house stoves were taken out in Germany. What is required of the house stove is that it should raise and keep the temperature of a room about 15° to 20°, and that as cheaply and conveniently as possible.

The usual plan of putting coal into house stoves is to do so after the fire has burned down, the result being that much combustible gas is distilled off, which thus produces waste of heat-giving material, besides using up part of the heat from another portion of the fuel for the distillation; and again when the heat rises sufficiently high to ignite these gases, a proper supply of air is frequently not allowed to enter the fire, so that much waste is caused by incomplete combustion, accompanied by the formation of soot and carbonic oxide.

The stove acts best when the fuel burns from above downwards, as the hydrocarbons which are distilled from the fresh coal at the bottom burn when they reach the top of the fire. Too much atmospheric air should, however, not be admitted.

The coal should be separated from the sides of the stove by a layer of fire-clay, to prevent loss of heat, and so to avoid the resulting loss of fuel from imperfect combustion. The habit of wetting the coal is a very objectionable one.

The author endeavoured to determine the loss of heat consequent on the above-mentioned conditions, employing different kinds of stoves, and different sorts of fuel. He analysed from time to time the gases which passed up the flue during the combustion, and noted the temperature in the flues and in the room, and the force of the current in the chimney. He embodies his results in a number of tables; as examples, the following are given.

In one experiment, calculating from the amount of air required to burn the fuel, the heat produced by the combustion, and that carried off by the flue gases, the author arrived at the conclusion that 40 per cent. of the total fuel value of the coal was carried off with the smoke gases, even when the fire was carefully managed.

In a second experiment, when the same coal and stove were employed, but in which the current of air in the flue was much increased, it was found that 80 per cent. of the heat was carried off by the smoke gases.

The third experiment was made with an iron stove, 0·5 meter high, lined with fire-proof stone, the smoke gases rising by one side of a partitioned pipe or trunk, nearly to the roof of the room, descending to the level of the stove by the other side, and again rising to the roof and making their escape into the chimney. All the joints about the stove were closed by a mixture of soluble glass, asbestos, and clay.

In this experiment, Piesberg anthracite was used as fuel, and the loss of heat, calculated as above mentioned, was 15 per cent. of the total fuel value of the coal. The temperature of the smoke at the fire-hole and at the exit into the chimney at the roof were measured by pyrometers, and the loss of heat which was given to the air of the room between these two points was very great.

The influence which the opening of the doors of the stove have on the loss of heat is great, as shown by the results obtained from burning coke in the iron stove. When the door of the ash-hole was partly opened, the loss amounted to 17 per cent., and when closed, to 6 per cent., but when the ash-hole door was completely opened, and the fire-place door partly opened, the combustion became very vigorous, the temperature of the gases in the flue rose rapidly, so that the thermometer had to be removed, whilst in proportion to the increased draught the amount of carbonic anhydride diminished, and the loss in heat corresponded to about 40 per cent. of the fuel value. The draught ranged between 2·5 and 4·4 mm. W. T.

**Salts obtained from the Mother-liquors of the Brine-springs of Volterra.** By A. FUNARO (*Gazzetta*, 9, 289—293).—In a note on these brine-springs (*Gazzetta*, 8, 71, and this Journal, Abst., 1878, 652) the author suggested that they might be utilised for the extraction of potash salts. Experiments have been made with this object, and analyses are given:—

1. Of the residue left on evaporating the mother-liquors.
2. Of the salt obtained by the evaporation of the mother-liquor to two-thirds of its volume.
3. Of the salt left on evaporating the mother-liquors from 2.
4. Of the salt obtained by lixiviating the residual salt with fresh mother-liquors, evaporating, again lixiviating the residue, and so on, by which means the proportion of sodium chloride is greatly diminished. In this way it is easy to obtain a salt containing 17—18 per cent. potassium sulphate, and consequently but little inferior to the "Kalialsalz" of Stassfurt. C. B. C.

**Lead Fume, and a New Process of Fume Condensing.** By A. FRENCH (*Chem. News*, 40, 163—166).—This paper describes a series of experiments made by the author and Messrs. H. J. and J. Wycliffe Wilson with a view to discover a good process for condensing fumes of lead, silver, and other metals, which volatilise in the smelting and refining operations. Not only does the loss of lead by sublimation amount to hundreds of tons in a year at many works, but the injury which is done to health and vegetation is very great. The various methods of condensing fumes which have been tried in this and other countries may be classed as follows:—

1. Deposition of the fume by its own gravity in long flues with or without the addition of a series of settling chambers, placed either near to or at some distance from the furnace.

2. Filtering through flues, towers, or chambers containing brush-wood, coke, coarsely woven fabric, or similar porous material, using water either in a constant or intermittent stream to keep the filters from becoming choked.

3. The use of water, either in the form of steam or in showers of drops or jets, projected with some considerable degree of force into and across the current of smoke.

4. Processes based on the inverse of the preceding principle, viz., passing the smoke under and through a depth of water, either in great volumes, as in the old Stagg's condenser, or in a more or less comminuted condition.

As to the physical nature of the lead fumes and their deportment under varying conditions of temperature and friction, experiments have proved that as the vaporised lead cools, it assumes the condition of a vast number of minute isolated particles. Lead fume appears to have no definite composition, as the proportions of its constituents vary in every specimen. The lead varies from 35—65 per cent. Lead fume, besides silver, invariably contains a little gold; usually from  $\frac{1}{2}$  to 1 per cent. of the quantity of silver. Platinum and iridium have also been found in the fumes on several occasions.

The greatest deposition of lead fume takes place, as might be expected, near the furnace, and the fume is most abundant whenever the gases have suffered the greatest friction and fall in temperature.

The author, in the next place, discusses the various methods of condensing fumes as classified in the above manner, and points out the objections they are subject to. He then describes a new apparatus for condensing these fumes. Copper-wire gauze, having about 15 meshes to a lineal inch, is used in the apparatus, the meshes being about one-twentieth of an inch wide. A number of gauze diaphragms are arranged one above the other in horizontal planes, and at small distances apart. The whole apparatus is submerged in water, the smoke being equally distributed under the diaphragms by means of a horizontal series of perforated pipes. The gauze diaphragms do not add much to the resistance which the smoke current has to overcome in its passage through the apparatus: three of the size mentioned above add about half an inch of water pressure. The depth of water usually employed is 7 inches above the perforated pipes, and with this depth the water-gauge indicates a resistance of about 10 inches, one half inch only of which is due to the gauze, the remainder being due to the depth to which the smoke depresses the water at the inlet passages. The ascending gases set up an upward current of water through the gauzes, and to promote a steady circulation of this, a return passage is provided. Each square foot of area of the diaphragm space is capable of passing about 40 cubic feet of smoke per minute, and when a blast furnace is employed for smelting lead-ore about 1 foot of area will be required for each ton of ore smelted in 24 hours.

During the past six months, almost daily assays have been made of the smoke before it entered and after it left the condensers at the

Sheffield Smelting Company's works. With a few exceptions these have exceeded 95 per cent. of fume caught. In a few cases as much as 99·5 per cent. of the metallic contents of the smoke has been caught. After the lead has been removed from the smoke, the large quantity of sulphurous acid which is usually contained in it may be recovered in a very simple manner. The gases can be mixed with a little air, if enough of oxygen is not already present, and then propelled by means of a steam jet through a heating apparatus similar to the hot blast heaters used in iron smelting works, and the hot sulphurous acid, steam, and air passed through common salt, according to Hargreave's process. By this means lead or copper smoke will be rendered not more pernicious than that from ordinary chimneys. Any arsenic or zinc which reaches the condenser is dissolved in the water, and thus separated from the lead fume, which subsides to the bottom. The apparatus was tried with hydrochloric acid vapour, and condensed 97·75 per cent.; of common salt vapour, it condensed 93 per cent.

A Root's blower is used with iron revolvers for forcing the smoke through the apparatus; from  $2\frac{1}{2}$  to 3-horse power is amply sufficient to work a condenser large enough for a furnace to smelt 15 tons of lead-ore per 24 hours. The weight of a condenser for that size of furnace is 18 cwts. The smoke should be cooled to about  $120-130^{\circ}$  F. by passing it through iron pipes, or any other kind of flue. This is necessary to prevent rapid evaporation of the water with which the condenser is supplied. It is also very important to cool the smoke as far as possible, so as to have a smaller volume to pass, and thereby save both power and cost of a larger apparatus. D. B.

**Preservation of Milk.** By E. KLEBS (*Dieb. Centr.*, 1879, 541).—The author heats the milk to a temperature of  $65-70^{\circ}$ , whereby the fresh taste is preserved. J. K. C.

**Composition of "Grains" from Malt.** By A. MARKL (*Dieb. Centr.*, 1879, 388).—Malt, weakly dried, gives "grains" richer in starch than when it has been more strongly dried. 100 parts of grains obtained by the infusion process contained:—

|             | Fresh.       |           |                      |
|-------------|--------------|-----------|----------------------|
|             | From gently. | Stronger. | Strongly dried malt. |
| Water.....  | 79·3         | 79·1      | 78·6                 |
| Albumin.... | 4·1          | 4·7       | 5·4                  |
| Fat .....   | 0·4          | 0·3       | 0·4                  |
| Fibre ..... | 6·2          | 7·8       | 9·4                  |
| Starch .... | 9·5          | 6·7       | 5·3                  |
| Ash .....   | 1·1          | 1·3       | 1·2                  |

J. K. C.

## General and Physical Chemistry.

**New Galvanic Couple.** By A. NIAUDET (*Compt. rend.*, 89, 703—708).—This couple consists of a plate of zinc for a positive, and a plate of carbon, surrounded with pieces of carbon, for a negative electrode: the former is immersed in a solution of common salt, and the latter in a solution of chloride of lime in a porous cell. The chloride of lime acts as a depolariser, the hydrogen decomposing the hypochlorous acid, forming water and hydrochloric acid, which unites with the zinc or lime, forming salts which are very soluble and good conductors. As zinc is not attacked by chloride of lime, the action takes place only when the circuit is closed; so that with a broken circuit, a couple may be kept for any length of time.

When sodium chloride is used, the electromotive force is greater than with any other solution, being 1.6 volts, and 1.5 after standing for some months. The depolarising action of chloride of lime is not complete, as is the case with copper sulphate, and with a slight external resistance the electromotive force slightly diminishes if the current continues; but it regains its former strength on standing. The internal resistance is reduced to a minimum by bringing the plates as close together as possible. To prevent the smell of the bleaching powder being disagreeable, the porous cell is closed with a cork.

L. T. O'S.

**Determination of the Density of Vapours which Attack Porcelain at a Red Heat.** By V. MEYER and H. ZUBLIN (*Ber.*, 12, 2204—2205).—The apparatus used for determining the vapour-density of those bodies which attack porcelain, consists of a platinum cylinder 245 mm. in length and 26 mm. diameter, to which is soldered, by means of the oxyhydrogen blowpipe, a platinum tube 400 mm. long and 7 mm. in diameter. To protect the cylinder from the action of the furnace-gases, which would permeate the platinum walls, it must be surrounded by a Berlin porcelain tube, glazed inside and out, 60 cm. long.

W. C. W.

**Specific Heats and Melting Points of the Refractory Metals.** By J. VIOLLE (*Compt. rend.*, 89, 702—703).—The specific heat of iridium, which has been determined up to a temperature of 1400°, is found to increase regularly with the temperature according to the formula  $C_p = 0.037 + 0.000006 t$ . The melting point determined by the calorimetric method (this Journal, *Abst.*, 1879, 294) is found to be 1950°.

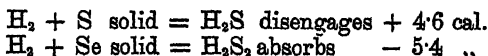
The specific heat of gold remains nearly constant between 0° and 600°, but increases constantly between 600° and its melting point: according to Regnault, the specific heat of gold = 0.0324 between 0° and 100°, and is nearly the same at 600°, but according to the author it is a little less at 100°, namely, 0.0316. At 900° it is 0.0345, and 0.0352 at 1020°.



The melting points of the different metals determined by the author are—

|                 |      |            |
|-----------------|------|------------|
| Silver .....    | 954° |            |
| Gold .....      | 1035 |            |
| Copper .....    | 1054 |            |
| Palladium ..... | 1500 |            |
| Platinum .....  | 1775 |            |
| Iridium .....   | 1950 | L. T. O'S. |

**Decomposition of Seleniuretted Hydrogen by Mercury.** By BERTHELOT (*Compt. rend.*, 89, 684).—Seleniuretted hydrogen, when kept in contact with mercury for some time at the ordinary temperature, is decomposed, with formation of mercuric selenide; under similar circumstances, sulphuretted hydrogen has no appreciable action on mercury, it being only at 550° that decomposition takes place. This difference may be due to the difference in the heat of formation of the two hydrides.

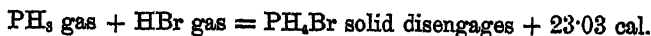


A similar case is met with when hydrobromic and hydrochloric acids are treated with mercury; the latter acid is decomposed only at high temperatures; the former slowly at the ordinary temperature, the heats of formation from the elements in the gaseous state being  $\text{HBr} = +13\cdot5$ ,  $\text{HCl} = +22$ .

In all such cases, the decomposed bodies being analogous and comparable with one another, their decomposition is easier the less heat disengaged in their initial formation. L. T. O'S.

**Combinations of Phosphine with the Haloid Acids.** By J. OGIER (*Compt. rend.*, 89, 705—708).—*Phosphine hydrochloride* (phosphonium chloride),  $\text{PH}_4\text{Cl}$ , is obtained by mixing equal volumes of phosphine and hydrochloric acid, at a temperature of 14°, and submitting them to a pressure of 20 atmospheres, when small crystals similar to those of the bromide deposit on the sides of the vessel. At 20° a liquid is obtained which, on cooling, deposits crystals. A mixture of equal volumes of the two gases under the ordinary pressure, deposits crystals when cooled to  $-30^\circ$  to  $-35^\circ$ .

*Phosphine hydrobromide* (phosphonium bromide),  $\text{PH}_4\text{Br}$ . The heat of formation of this body is measured by decomposing it with water, when  $\text{PH}_3\text{HBr} + \text{water} = \text{PH}_3 \text{ gas} + \text{HBr dissolved}$ , absorbs  $-3\cdot03$  cal. By deducting from this number, representing the thermal action of water on 1 equiv. of  $\text{PH}_4\text{Br}$ , the heat of solution of hydrobromic acid in water ( $+20\cdot0$ ), and changing the signs, the heat disengaged by the union of the two gaseous bodies is obtained.

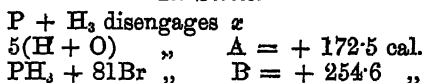


*Phosphine hydriodide* (phosphonium iodide),  $\text{PH}_4\text{I}$ . The heat of formation of this body is determined like that of the hydrobromide,  $\text{PH}_3\text{HI} + \text{water} = \text{PH}_3 + \text{HI dissolved}$ , absorbs  $-4\cdot77$  cal. By deducting the heat of solution of HI in water and changing the sign,

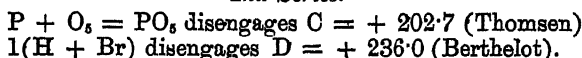
we get  $\text{PH}_3$  gas +  $\text{HI}$  gas =  $\text{PH}_4\text{I}$  solid disengages + 24.17 cal. By directly measuring the heat evolved by the union of the two gases, +24.2 cal. was obtained.

The author corrects an error made in the calculation of the heat developed in the formation of phosphine (*ibid.*, 87, 210, and this Journal, Abst., 5, 1879) due to the heat of formation of *gaseous* water instead of *solid* water being used. The corrected calculation stands thus:—

1st Series.

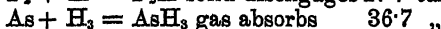


2nd Series.

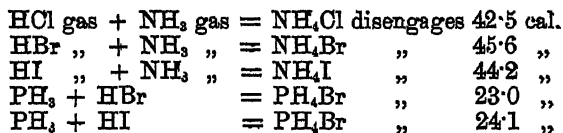


From which  $x = (\text{C} + \text{D}) - (\text{A} + \text{B}) = + 11.6$  cal., therefore  
 $\text{P} + \text{H}_2 = \text{PH}_3$  gas disengages + 11.6 cal.

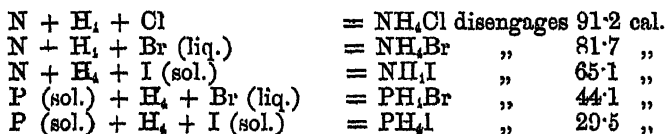
Similarly,  $\text{P}_2 + \text{H}_2 = \text{P}_2\text{H}$  solid disengages 17.7 cal.



The heat of formation of phosphine is less than that of ammonia. By comparing the heats of formation of ammonia and phosphine compounds we find—



Starting from the elements themselves, we get—

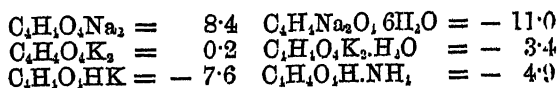


The heat developed by the formation of ammonium cyanide and ammonium sulphide are—



As a reducing agent, phosphine hydride is not as effectual in some cases as hydriodic acid, on account of the loss of energy which takes place in its formation. L. T. O'S.

**Thermic Study of Succinic Acid.** By P. CHEROUSTCHOFF (*Compt. rend.*, 89, 579—582).—The following numbers represent the heat evolved by various salts of succinic acid when dissolved in 400 c.c. of water:—



From these may be calculated the heat evolved by the combination of the solid salt with water. In the case of the soda salt, it becomes 10.8; with the potash salt, 2.2 units. Succinic acid dried at  $110^\circ$  gives by solution in 500 c.c. at  $11^\circ$  an absorption of heat equal to 6.4 units.

The heat of neutralisation by alkalis made with a solution containing  $\frac{1}{4}$  of an equivalent of acid gave as follows, everything being dissolved, and remaining dissolved:—

With soda 26.4; with potash 26.4; with ammonia 22.9.

By increasing the relative proportions of succinic acid to alkali, the numbers were slightly altered: thus with 2 mols. of acid to 2 mols. of potash, 27.25 units were obtained; with 3 mols. of acid to 2 mols. of potash, 24.76 units; with 2 mols. of acid to 2 mols. of ammonia, 24.7 units.

The number found by Thomsen for the heat of neutralisation of succinic acid was 24.8 units; the author considers that this number is incorrect. The foregoing numbers may, if required, be referred to a reaction between the solid constituents.

With soda 40.02; with potash 46.37; with ammonia gas 39.42.

As regards the amount of heat evolved on neutralisation, succinic acid occupies a position intermediate between benzoic and tartaric acids.

|                                   | NaHO. | KHO.  | NH <sub>3</sub> gas. |
|-----------------------------------|-------|-------|----------------------|
| Acetic acid.....                  | 18.3  | 21.9  | 18.5                 |
| Benzoic acid .....                | 17.4  | 22.5  | 17.0                 |
| $\frac{1}{2}$ succinic acid ..... | 20.01 | 23.19 | 19.7                 |
| $\frac{1}{2}$ oxalic acid .....   | 26.5  | 29.4  | 24.4                 |
| $\frac{1}{2}$ tartaric acid ..... | 22.9  | 27.1  | —                    |
| Sulphuric „ .....                 | 34.7  | 40.7  | 33.8                 |

By determining the heat of solution of the anhydride, and of the hydrated acid in potash, the heat of combination of the anhydride with water was obtained by difference:  $\text{C}_4\text{H}_2\text{O}_4 = 20.06$ ;  $\text{C}_4\text{H}_4\text{O}_4 = 29.78$ ; difference = 9.72 units.

If the heat of solution of the hydrated acid in water be deducted from the heat of solution of the same acid in potash, the number of units obtained should be equal to the heat of neutralisation by potash in solution.

Heat evolved on solution in potash = + 20.06  
 „ „ „ water = - 6.4

Difference = 26.46

This indirect verification of the number 26.4 supports the author's results as against Thomsen's figure, 24.8.

Succinic acid appears to be completely displaced from its combinations by sulphuric acid; but doubtful results only were obtained in the case of hydrochloric acid, further data are in fact required respecting the heat evolved or absorbed in diluting succinic acid and its salts.

J. W.

## Inorganic Chemistry.

**Silicon Nitride.** By P. SCHÜTZENBERGER (*Compt. rend.*, 89, 644—646).—The composition of the silicon nitrides discovered by Sainte-Claire Deville and Wöhler, not having been experimentally determined, the author has sought to prove the existence of two compounds by the following experiments:—

By heating crystallised silica with gas carbon in a blast furnace for some time, a mass is obtained consisting of unaltered silica, a white substance soluble in cold concentrated hydrofluoric acid without evolution of gas, and a green substance which is insoluble in hydrofluoric acid and caustic alkalis, and, after successive treatment with hydrofluoric acid and dilute potash, is obtained as a green infusible powder: this is not attacked by water or by solution of caustic alkalis, but is dissolved by potash at a red heat with formation of potassium silicate and evolution of hydrogen and ammonia. The analyses agree with the formula  $(\text{SiN})_2$ .

The white substance soluble in hydrofluoric acid cannot be obtained in the pure state, but most probably it has the formula  $\text{Si}_3\text{N}_4$ ; this is rendered probable by the fact that on heating  $(\text{SiN})_2$  in a current of chlorine, it loses 22 per cent. of its weight of silicon, and a white substance, soluble in hydrofluoric acid, is left. The equation,  $(\text{SiN})_2 + \text{Cl}_2 = \text{SiCl}_4 + \text{Si}_3\text{N}_4$ , represents the loss of 22.4 per cent. of silicon.

By passing ammonia gas into a flask containing silicon tetrachloride, a very light white powder is obtained soluble in water with separation of  $\text{Si}(\text{HO})_4$ ; when heated in a current of hydrogen, ammonium chloride sublimes. The results of analyses compare fairly with those required by the formula  $\text{Si}_3\text{N}_4\text{Cl}_2\text{H}$ . Its formation may be expressed thus:  $8\text{SiCl}_4 + 10\text{NH}_3 = \text{Si}_3\text{N}_4\text{Cl}_2\text{H} + 29\text{HCl}$ , and its decomposition by water, thus:  $\text{Si}_3\text{N}_4\text{Cl}_2\text{H} + 16\text{H}_2\text{O} = 8\text{SiO}_2 + 10\text{NH}_3 + 3\text{HCl}$ . When heated to bright redness in a current of ammonia, a white powder is obtained which is not attacked by water, and only slightly soluble in alkalis; its formula is  $\text{Si}_3\text{N}_4\text{H}$ . These experiments show the existence of two silicon nitrides, one  $(\text{SiN})_2$  corresponding to CN, the other probably of the formula  $\text{Si}_3\text{N}_4$ .

L. T. O'S.

**Action of Metallic Nitrates on Nitric Acid.** By A. DITTE (*Compt. rend.*, 89, 576—579).—Ammonium nitrate dissolves readily in fuming nitric acid, forming a liquid which does not solidify at  $5^\circ$ ; below this temperature crystallisation takes place, when the thermometer immediately rises to  $18^\circ$ . The crystals melt regularly at  $18^\circ$ , but generally exhibit the phenomenon of surfusion, in which condition

a crystal of ammonium nitrate will *not* determine solidification. The composition of the salt is  $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$ ; when melted the liquid closely resembles nitric acid, but does not fume in the air; it is capable of dissolving a large quantity of ammonium nitrate to form the salt  $\text{NH}_4\text{NO}_3 \cdot \text{HNO}_3$ , melting at  $9^\circ$ ; this latter remains liquid at  $4^\circ$ , and a crystal of the di-acid salt does not induce crystallisation. The same compounds are produced when dry ammonium nitrate is placed in an atmosphere containing nitric acid vapour.

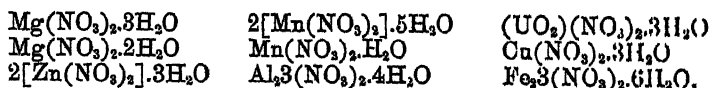
Potassium nitrate, in like manner, produces the salt  $\text{KNO}_3 \cdot 2\text{HNO}_3$ , melting at  $-3^\circ$ ; when carefully cooled the whole will remain liquid at  $-10^\circ$ , but the temperature rises to  $-3^\circ$  as soon as crystallisation sets in. The monacid salt,  $\text{KNO}_3 \cdot \text{HNO}_3$ , could not be prepared. Thallium and rubidium nitrates also combine with nitric acid to form the salts  $\text{TlNO}_3 \cdot 3\text{HNO}_3$  and  $\text{RbNO}_3 \cdot 5\text{HNO}_3$  respectively; their melting points are not given, but in general properties they resemble the potassium and ammonium salts previously described. J. W.

**Action of Metallic Nitrates on Nitric Acid.** By A. DITTE (*Compt. rend.*, 89, 641—643).—The author has shown (see previous abstract) that certain metallic nitrates combine with nitric acid to form acid salts. There are, however, other salts which behave differently. Magnesium nitrate,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , for example, which contains 6 mols. of water of crystallisation, melts and begins to decompose when heated; under certain circumstances, however, when heated, it yields a syrupy mass, which suddenly solidifies, evolving a large amount of heat; it consists of  $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . It is decomposed by heat, leaving a residue, from which is separated by water a nitrate having the composition  $\text{MgO} \cdot \text{Mg}(\text{NO}_3)_2$ ; this decomposes without melting, leaving magnesia.

If the decomposition of the neutral nitrate be stopped the moment nitric oxide begins to be evolved, a deliquescent mass is obtained, which dissolves in nitric acid, and on cooling deposits transparent prisms, consisting of  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

The basic nitrate, when treated with nitric acid, yields the neutral salt, but owing to the quantity of water set free it is impossible to obtain acid salts; the author therefore proposes to saturate a solution of the neutral salt with nitric anhydride, which will combine with the water, and thus a solution of the anhydrous salt in nitric acid will be obtained.

To this group besides magnesium nitrate belong the nitrates of manganese, aluminium, zinc, uranium, copper, and iron, which give the following salts:—



Of these, the nitrates of manganese, aluminium, and iron leave a residue of oxide when heated; the others yield basic nitrates.

Secondly, there exists a class of nitrates which are insoluble, or only sparingly soluble in nitric acid, to which belong the nitrates of

sodium, lithium, calcium, strontium, barium, nickel, cobalt, bismuth, cadmium, mercury, and silver. L. T. O'S.

**Contributions to our Knowledge of Clays and Earthenware Goods.** (*Dingl. polyt. J.*, 234, 465—473).—Bischof mentions a new source of bauxite at Kleinsteinheim, in the Offenbach district. The following is the composition:—

| $\text{Al}_2\text{O}_3$ . | $\text{SiO}_2$ . | $\text{Fe}_2\text{O}_3$ . | Loss on ignition. |
|---------------------------|------------------|---------------------------|-------------------|
| 56.02                     | 10.97            | 6.19                      | 26.42 = 99.60     |

Leger gives the following analyses (p. 156) of clay substances used for the preparation of fine white goods. A and B are French goods, C and D are Belgian goods, the former being used for fine goods, the latter for ordinary; and E is German.

Lindhorst states that, besides lime and the flue gases, the alumina and alkalis contained in clay also influence the coloration of clay; whereas gypsum is inactive. Experiments were made with various oxides, the colour produced being red with iron, green with chromium, grey with copper, white with zinc, yellowish-grey with nickel, brown with manganese, pink to violet with gold, and greyish-white with platinum. Mixtures of these substances produce intermediate shades. The black-burning of Indian goods is explained by Sarnow as follows:—When earthenware goods are polished by rubbing them, the surface of the clay is rendered more compact; by subsequently placing the clay in a sooty atmosphere, and exposing it to a temperature high enough to expel the combined water, the pores produced are filled with coal. The latter cannot ignite in a reducing atmosphere, and becomes fixed in the pores as the clay shrinks. A shining mass is produced, which is so dense that it resists even the penetration of water.

D. B.

**Ultramarine.** By KNAPP (*Dingl. polyt. J.*, 234, 479—486).—In the first part of his investigation of this subject (*ibid.*, 229, 69, 173), the author considered mainly the changes taking place during the formation of ultramarine, and its subsequent conversion into blue. The object of the present paper is to consider the cases, which, although not strictly connected with ultramarine, represent properties common to the same. These are well known, and the author merely mentions a few instances, which have not yet been noticed.

Dressel found that noscan assumed a pure blue colour, when heated with coal. (Noscan is a mixture of hatyne and sodalite.) During the fusion of borax with sodium sulphide, i.e., the yellow colouring of glass, it was noticed that after the addition of boracic acid to the fused mass, a black product was formed, which on continued heating assumed a blue colour. The same colour was produced when potassium thiocyanate was fused, and also when sulphur was introduced into potassium cyanide and the mixture heated. The formation of blue with fused borax led to the following important deductions:—1. Silicic acid can be replaced by boracic acid, in order to produce the blue. 2. The borate gives a blue as stable in properties as the silicate. 3. The blue of the borate is not altered by fusion, its melting point being high

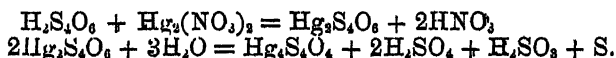
| Constituents.             | Total A. |       | Not decomposable by $H_2SO_4$ (Quartz + Feldspar). |       | Decomposable by $H_2SO_4$ (Calculated on 100). |        | Total B. |       | Not decomposable by $H_2SO_4$ (Quartz + Feldspar). |       | Decomposable by $H_2SO_4$ (Calculated on 100). |        | Total C. |       | Not decomposable by $H_2SO_4$ (Quartz + Feldspar). |       | Decomposable by $H_2SO_4$ (Calculated on 100). |      | Total D. |   | Not decomposable by $H_2SO_4$ (Quartz + Feldspar). |   | Decomposable by $H_2SO_4$ (Calculated on 100). |   | Total E. |   | Not decomposable by $H_2SO_4$ (Quartz + Feldspar). |   | Decomposable by $H_2SO_4$ (Calculated on 100). |   |
|---------------------------|----------|-------|--|-------|--|--------|----------|-------|--|-------|--|--------|----------|-------|--|-------|--|------|----------|---|--|---|--|---|----------|---|--|---|--|---|
|                           | 9.24     | 0     | 13.64  | 0     | 0  | 0      | 13.61    | 7.24  | 0  | 0     | 0  | 0      | 0        | 0     | 0  | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $SiO_2$ .....             | 19       | 71.17 | 29.87  | 47.00 | 67.45  | 43.24  | 45.56    | 65.02 | 37.87  | 47.89 | 61.70  | 29.97  | 46.13    | 64.25 | 40.79  | 45.39 | 38.03  | 1.04 | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $Al_2O_3$ .....           | 26.69    | 1.89  | 87.85  | 21.59 | 1.89   | 37.07  | 23.82    | 2.14  | 86.00  | 27.01 | 0.74   | 88.17  | 21.46    | 1.78  | 88.03  | 1.04  | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $Fe_2O_3$ .....           | 1.14     | 0     | 1.63   | 0.59  | 0  | 1.11   | 0.59     | 0     | 1.01   | 0.61  | 0  | 0.89   | 0.54     | 0     | 0  | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $CaO$ .....               | trace    | 0     | trace  | 0     | 0  | 0      | trace    | 0     | trace  | 0.38  | 0.25   | 0      | 0.94     | 2.38  | (2.38)   | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $MgO$ .....               | 0.06     | 0     | 0.09   | 0.51  | 0  | 0.99   | 0.22     | 0     | 0  | 0.38  | 0.25   | 0      | 0.65     | 0     | 0  | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $K_2O$ .....              | 1.30     | 1.01  | 0.42   | 1.92  | 1.26   | 1.24   | 1.43     | 1.43  | 1.43   | 1.11  | 1.32   | 0.50   | 2.16     | 1.97  | 1.09   | 8.69  | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $Na_2O$ .....             | 0        | —     | —  | 0.24  | —  | 0.45   | 0.60     | —     | —  | —     | 0.67   | —      | —        | —     | —  | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |
| $CO_2$ .....              | 0        | —     | —  | 0     | 0  | 0      | 0        | 0     | 0  | 0     | 0  | 0      | 0        | 0     | 0  | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| $H_2O$ organic substance. | 9.24     | 0     | 13.64  | 7.23  | 0  | 13.61  | 7.24     | 0     | 12.37  | 8.11  | 0  | 11.77  | 6.12     | 0     | 11.83  | 0     | 0  | 0    | 0        | 0 | 0  | 0 | 0  | 0 | 0        | 0 | 0  | 0 | 0  | 0 |
| Clay substance.....       | 100.14   | 32.27 | 100.16   | 99.53 | 46.89  | 100.00 | 99.37    | 41.44 | 99.76  | 1.03  | 31.21  | 100.12 | 99.74    | 43.66 | 99.98  | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |
| Quartz .....              | —        | 67.73 | —  | —     | 53.61  | —      | —        | 53.56 | —  | —     | —  | 68.79  | —        | —     | 51.97  | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |
| Feldspar .....            | —        | 24.63 | —  | —     | 36.75  | —      | —        | 30.26 | —  | —     | —  | 27.38  | —        | —     | 34.50  | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |
| Calcium carbonate ....    | —        | 7.64  | —  | —     | 9.73   | —      | —        | 11.05 | —  | —     | —  | 3.83   | —        | —     | 9.16   | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |
|                           | —        | 0     | —  | —     | 0  | —      | —        | 0     | —  | —     | —  | 0      | —        | —     | 4.37   | —     | —  | —    | —        | — | —  | — | —  | — | —        | — | —  | — | —  | — |

enough to avoid the destruction of colour. 4. Alumina is not absolutely requisite for developing the blue colour. Silica without alumina, and alumina without silica form the blue colour. Besides these, other bodies gave similar results, *e.g.*, aluminium borate, calcium phosphate, and stannic oxide produce the blue colour. D. B.

**Erbium.** By P. T. CLÈVE (*Compt. rend.*, 89, 708—709).—This is an acknowledgment of Soret's claims to priority in the discovery published by the author (*ibid.*, 15th September, 1879). He points out that the substance called by him *holmium* is the same as that called *æ* by Soret. L. T. O'S.

**Tungsten Bronze.** By J. PHILIPP and P. SCHWEREL (*Ber.*, 12, 2234—2236).—Although tungsten bronze (the golden-yellow compound obtained by fusing acid sodium tungstate in a current of hydrogen) resists the action of acids and of alkalis, it is readily decomposed by an ammoniacal solution of silver nitrate. By making use of this fact in analysing the substance, the authors find that its composition is  $\text{NaWO}_3$ , instead of  $\text{Na}_2\text{WO}_4 + \text{W}_2\text{O}_5$ , as stated by Malaguti (*Ann. Chim. Phys.*, 60, 284). W. C. W.

**New Basic Salts of Mercuric Sulphide.** By W. SPRING (*Annalen*, 199, 116—126).—The yellow amorphous substance, which is precipitated on the addition of mercurous nitrate to an aqueous solution of tetrathionic acid (Wachenroder, *Annalen*, 60, 190), has, after drying and treatment with carbon bisulphide, the composition  $\text{Hg}_4\text{S}_4\text{O}_4$ . Its formation is due to the following reactions:—

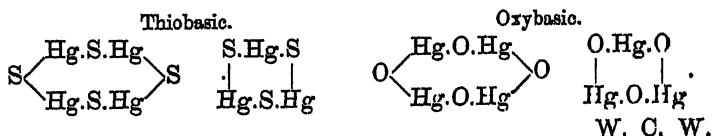


When perfectly free from tetrathionic acid, this substance undergoes no change on exposure to the light or to a temperature of  $120^\circ$ . The amount of heat evolved on treating this body with sodium sulphide shows that it is not a mixture of mercuric sulphide and sulphate, but a definite compound, *viz.*, *trithiobasic mercuric sulphate*. The salt is insoluble in water and in most acids. It is soluble in *aqua regia* and in a mixture of hydrochloric acid and bromine, and it is converted by the action of warm nitric acid into a white insoluble salt, *monothiobasic trimercuric sulphate*,  $\text{HgS}(\text{HgSO}_4)_3$ .

Trithiobasic mercuric sulphate is decomposed by alkaline solutions, forming black mercuric sulphide. On boiling with barium nitrate, mercuric sulphide and barium sulphate are obtained. When the salt is boiled in water, sulphuric acid passes into solution and a dark yellow product remains, which has the composition  $(\text{HgS})_3\text{HgO}$ . Trithiobasic mercuric oxide turns black, and evolves sulphuretted hydrogen when brought in contact with dilute hydrochloric acid.

It is suggested that, for the purpose of classification, the basic mercuric sulphates may be considered to be derived from the following types, in which the O or S is replaced by the group  $\text{SO}_4$ .





**Oxidation of Gold by Galvanic Action.** By BERTHLOT (*Compt. rend.*, 89, 683—684).—Grotthuss (*Ann. Chim. Phys.*, 58, 60) observed that a gold wire is dissolved when employed as the positive terminal of a circuit in sulphuric acid. The author confirms these results, and shows that under similar circumstances nitric acid also dissolves gold. This is due neither to ozone nor, as suggested by Chevreul, to persulphuric acid, for neither of them has any action on gold.

L. T. O'S.

## Organic Chemistry.

**Normal Paraffins.** By C. SCHORLEMMER (*Annalen*, 199, 139—144).—By chlorinating pure hexane (from secondary hexyl iodide prepared by the action of hydriodic acid on mannitol), a mixture of monochlorides is obtained (b. p. 121—134°), which yields hexylene and ethyl-hexyl ethers on decomposition with alcoholic potash. The olefine combines with hydrochloric acid at the ordinary temperature, forming a chloride which boils at 124° without decomposition; whilst, according to Morgan (*Ann.*, 161, 275), the corresponding chloride from petroleum boils at 116° with decomposition. The acetate from the chloride yields an alcohol boiling at 130—135° and another at 135—140°, which split up on oxidation into acetic and butyric acids; propionic acid could not be detected.

The fact that the paraffins from petroleum have a higher specific gravity than those from other sources, and that the specific gravity diminishes when a portion of the hydrocarbon is oxidised by nitric acid, indicates that the normal paraffins from petroleum probably consist of a complicated mixture of homologous and isomeric hydrocarbons.

W. C. W.

**Constitution of Dibrom-ethylene.** By E. DEMOLE (*Ber.*, 12, 2245—2247).—By the action of aluminium chloride on a solution of dibromethylene in benzene, *unsymmetrical diphenylethylene*,  $\text{ClH}_2:\text{ClPh}_2$ , b. p. 174—176°, and a liquid boiling above 350°, are formed. The production of the former hydrocarbon shows that dibromethylene is also unsymmetrical,  $\text{Br}_2\text{C}:\text{CH}_2$ . This result agrees with the conclusions arrived at by Anschütz (*Ber.*, 12, 2073).

W. C. W.

**Glucose.** By FRANCHIMONT (*Compt. rend.*, 89, 713—714).—In applying Liebermann's method for the preparation of the acetyl derivatives of the phenols to the carbohydrates, the author obtained with

glucose a crystalline acetyl compound soluble in benzene, alcohol, acetic anhydride, and acetic acid; sparingly soluble in ether and in petroleum spirit, and insoluble in water. It is octo-acetyl diglucose,  $C_{12}H_{11}O_3(C_2H_3O_2)_8$ , (m. p.  $100^\circ$ ). It has a bitter taste, is dextrorotatory, and unlike glucose it is oxidised only with great difficulty; boiling chromic mixture does not attack it, and phosphorus pentachloride acts on it but slowly.

L. T. O'S.

**Cellulose.** By FRANCHIMONT (*Compt. rend.*, 89, 711—712).—Not being able to obtain any reaction between cellulose, acetic anhydride, and sodium acetate, the author substituted concentrated sulphuric acid for the last substance, when a violent reaction set in, and the cellulose was dissolved, the solution becoming coloured. On adding water to the solution, a white precipitate is formed, which is filtered and washed with cold alcohol until the washings are no longer coloured. The residue is then dissolved in hot alcohol, and from the solution microscopic needles or plates separate out (m. p.  $212^\circ$ ). These are soluble in benzene, sparingly soluble in cold alcohol, and insoluble in ether. It has the empirical formula  $C_{40}H_{54}O_{27}$ , and appears to be a derivative of triglucose, containing the acetyl-group eleven times. An acetyl-derivative is also obtained by substituting zinc chloride for sulphuric acid. This corresponds with a triacetyl-compound, but it is more probable that it is a saturated acetyl-derivative of  $n$ -molecules of glucose  $-(n-1)OH_2$ . It has not yet been identified with Schutzenberger's triacetyl-cellulose. The author has applied the same reaction to other carbohydrates.

L. T. O'S.

**Commercial Trimethylamine.** By E. DUVILLIER and A. BUISSE (*Compt. rend.*, 89, 709—711).—To detect the presence of ethylamine in commercial trimethylamine, which escaped the authors' notice in their previous research (this Journal, Abst., 1879, 912), from being present only in very small quantity (2 per cent.); the mother-liquors from the purification of the oxamides are decomposed with potash and the bases converted into sulphates; these are treated with absolute alcohol, which dissolves, all with the exception of monomethylamine sulphate. The soluble sulphates are distilled with potash, the bases collected over absolute alcohol, and the solutions treated with oxalic ether. The oxamic ethers are decomposed with lime, when crystals of calcium monothiooxamate separate out. This is the sixth base found in commercial trimethylamine. The authors also reply to Vincent's remarks (this Journal, Abst., 1879, 913) on their previous publication.

L. T. O'S.

**Ethylamine.** By H. KÖHLER (*Ber.*, 12, 2208—2211).—When a solution of mercuric chloride is boiled with ethylamine and the hot mixture filtered, the filtrate deposits on cooling white pearly scales, which have the composition  $Cl.HgNH_2Et$ . The insoluble precipitate which is formed at the same time is converted by boiling with water into yellow oxymercurethylamine chloride,  $Cl.Hg.O.HgNH_2Et$ .

Hence it appears that the action of ethylamine on mercuric chloride

is analogous to that of ammonia; the product, however, is much more readily oxidisable than is the case with white precipitate.

W. C. W.

**Action of Potassium Dichromate on Acetic Acid and Potassium Acetate.** By L. DANESI (*Gazzetta*, 9, 420—421).—The author finds that, when acetic acid is boiled with a solution of potassium dichromate, the acid is oxidised at the expense of the chromic acid, and carbonic anhydride is produced. In one experiment, the author employed equal weights of potassium dichromate and acetic acid; the latter diluted with water, but how much is not stated. The dichromate acts on potassium acetate in a similar manner, the chromic acid liberating acetic acid, which is subsequently oxidised.

C. E. G.

**Action of Hypochlorous Acid on Acrylic Acid.** By P. MELIKOFF (*Ber.*, 12, 2227—2228).—The monochlorolactic acid obtained by the action of hypochlorous acid on a dilute aqueous solution of acrylic acid and the acid formed by treating glyceric acid with hydrochloric acid (*Ber.*, 12, 178, this Journal, Abstr., 1879, 521) are shown to be identical, by a comparison of their amido-derivatives and of their barium and tin salts (both of which are amorphous). The amido-acid, which is produced by heating ethyl chlorolactate and ammonia at 120°, crystallises in long, thin prisms, and also in four-sided plates. It resembles serine in most of its properties, but is somewhat less soluble in water.

W. C. W.

**Acetylenedicarboxylic Acid.** By E. BANDROWSKI (*Ber.*, 12, 2212—2216).—Copper acetylenedicarboxylate,  $\text{CuC}_2\text{O}_4 + 3\text{H}_2\text{O}$ , forms glistening blue scales, which are sparingly soluble in cold water, and are decomposed by hot water. This salt slowly undergoes decomposition at the ordinary temperature. The silver salt dissolves in strong nitric acid, but the solution rapidly becomes turbid, owing to the deposition of silver cyanide.

Acetylenedicarboxylic acid is converted into succinic acid by the action of nascent hydrogen. When heated with water, it splits up according to the equation  $\text{C}_4\text{H}_2\text{O}_4 = \text{CO}_2 + \text{C}_3\text{H}_4\text{O}_4$ . The new acid melts at 145°, and is soluble in water, alcohol, and ether. It is crystalline, and forms well crystallised salts.

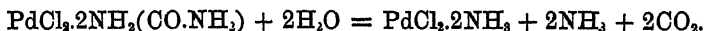
When bromine is added to an aqueous solution of acetylenedicarboxylic acid, the dibromo-acid,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4$ , is formed, together with small quantities of bromoform, and a crystalline compound of unknown composition.

Dibromacetylenedicarboxylic acid is deposited from its aqueous solution in transparent crystals, which dissolve freely in ether and in alcohol. The silver salt,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4\text{Ag}_2 + \frac{1}{2}\text{H}_2\text{O}$ , crystallises in small needles, which explode when heated. The lead salt,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4\text{Pb}$ , also forms needles which are soluble in water. The acid begins to blacken at 217°, and melts with decomposition at 220°. On distillation it yields hydrobromic acid and Kekulé's dibromomaleic acid (m. p. 108°) (*Annalen*, 130, 3), hence it may be regarded as dibromofumaric acid.

Attempts to prepare tetrabromosuccinic acid by the action of bromine on acetylenedicarboxylic acid were unsuccessful.

W. C. W.

**Carbamido-palladious Chloride, or Palladoso-uramionium Chloride.** By E. DRECHSEL (*J. pr. Chem.*, 20, 469—475).—This substance is obtained by mixing solutions of palladious chloride and urea. It forms a brownish crystalline powder, sparingly soluble in water, and has the formula  $\text{PdCl}_2 \cdot 2\text{CN}_2\text{H}_4\text{O} = \text{Pd}[\text{NH}_2(\text{CO} \cdot \text{NH}_2)\text{Cl}]_2$ . As it is nearly insoluble in water, attempts were made to found a method of estimating urea and palladium by its formation, but with no success in the former, and unsatisfactory results in the latter case. When boiled with water, it undergoes the following decomposition:—



When evaporated with excess of palladious chloride, the urea appears to be partially decomposed with formation of free cyanic acid. Some urea combining with the cyanic acid, biuret is produced:—



An attempt was made to prepare hydantoic acid by evaporating glycocine with carbamido-palladious chloride, but without success. Besides small quantities of biuret, urea hydrochloride, and palladium bases, palladious amidoacetate was formed. No hydantoic acid could be detected.

W. R.

**Relative Displaceability of Bromine in the Monobromobenzyl Bromides.** By C. L. JACKSON (*Ber.*, 12, 2243—2245).—When sodium acetate acts on the ortho-, meta-, and para-monobromobenzyl bromides under similar conditions, the bromine replaced in these compounds in a given time is in the ratio 52 : 77 : 100.

W. C. W.

**Tolylphenol.** By G. MAZZARA (*Gazzetta*, 9, 421—423).—The xylene employed for the preparation of the tolyl chloride is obtained from commercial xylene by fractional distillation, and agitating the portion boiling at 136—139° with concentrated sulphuric acid. On redistilling the undissolved hydrocarbon, it yields a fraction boiling at 137—139°, which is treated with chlorine while boiling to convert it into tolyl chloride (b. p. 190—195°). When equal parts of tolyl chloride and phenol are heated with zinc filings, a violent reaction takes place, with evolution of hydrochloric acid and formation of tolylphenol,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Me}$ , which may be separated from the product by fractional distillation. It is a colourless liquid of feeble odour, boiling at 250—255° under a pressure of 8—10 mm. It is insoluble in water, but dissolves in alcohol, ether, chloroform, and alkaline solutions. It gives no coloration with ferric salts. When tolylphenol is treated with acetic chloride, it yields an acetate,



This is a colourless liquid, boiling at 250° under a pressure of 9 mm., and decomposing on exposure to moist air, with formation of tolylphenol and acetic acid.

C. E. G.

**Action of Nitrosodimethylaniline on Phenols which do not contain the Methyl Group.** By R. MELDOLA (*Ber.*, 12, 2065—2066).—When nitrosodimethylaniline hydrochloride (1 mol.) is slowly added to a solution of  $\beta$ -naphthol (1 mol.) in glacial acetic acid at  $110^\circ$ , a blue mass is produced. This is washed with water, dissolved in hot alcohol, and mixed with hydrochloric acid. On cooling, bronze-coloured needles are deposited, which dissolve in alcohol and in water, forming a bluish-violet solution.

Similar compounds are obtained by the action of nitrosodimethylaniline on resorcinol and on  $\alpha$ -naphthol. W. C. W.

**Action of Ferric Chloride on Orthodiamidobenzene.** By C. RUDOLPH (*Ber.*, 12, 2211—2212).—By the action of ferric chloride on orthodiamidobenzene, a hydrochloride is formed which has the composition  $C_6H_8N_6O.2HCl.5H_2O$ . The base combines with sulphuric acid, yielding several different salts. The formula of the neutral sulphate is  $C_{12}H_{18}N_6O.H_2SO_4.3H_2O$ . W. C. W.

**Tolylenediamines.** By R. NIETZKI (*Ber.*, 12, 2236—2238).—Paradiamidotoluene (m. p.  $64^\circ$ ) from nitro-orthetoluidine (m. p.  $130^\circ$ ) is identical with the tollylenediamine from amidooztoluene. The para-diamines can be distinguished from the ortho- and meta-diamines by their forming quinones on oxidation with ferric chloride, whilst the ortho-compounds yield a coloured crystalline precipitate having a metallic lustre.

When treated with nitrous acid, para-diamines form diazo-compounds, whilst the meta-derivatives yield colouring matters analogous to phenylene brown, and the ortho-diamines give colourless stable compounds containing nitrogen. W. C. W.

**Occurrence of Paraleucaniline in the Manufacture of Rosaniline.** By O. GRAEBE (*Ber.*, 12, 2241—2242).—Considerable quantities of paraleucaniline are found in the rosaniline manufacture in the mother liquors from which the chrysaniline has been precipitated. Whether leucaniline is the first product of the reaction of arsenic acid on a mixture of aniline and toluidine (the colouring matters being afterwards formed by oxidation), or whether it owes its origin to the reduction of parrosaniline is uncertain, but the author considers the first hypothesis the more probable. W. C. W.

**Dimethylphenyl Glycocine or Phenylbetaine.** By J. ZIMMERMANN (*Ber.*, 12, 2206—2207).—*Phenylbetaine hydrochloride*,



formed by digesting an ethereal solution of dimethylaniline (2 mols.) with monochloroacetic acid (1 mol.) can be obtained in white needles by adding ether to the concentrated aqueous solution of the compound. The platinochloride forms beautiful dark red crystals.

*Phenylbetaine ethylchloride*,  $\begin{array}{c} CH_3 \\ | \\ \text{N} \cdot (Me)_2 \\ | \\ CO_2 \end{array} \text{PhEtCl}$ , is deposited in hygroscopic crystals when a mixture of ethyl monochloroacetate and

dimethylaniline is heated at 100° for four hours. On treatment with silver oxide, the chlorine is eliminated from this substance, and a powerful base is produced, which is very deliquescent, and does not appear to form crystalline salts. W. C. W.

**Hydroxyazobenzene and Paramethylhydroxyazobenzene.** By G. MAZZARA (*Gazzetta*, 9, 424—425).—*Hydroxyazobenzene* or *phenoldiazobenzene*,  $C_{12}H_{10}N_2O$ , has already been obtained by Griess (*Annalen*, 137, 84), and by Kekulé and Haged (*Ber.*, 4, 233). The author finds that the most convenient mode of preparation is to dissolve 3 parts of potassium nitrite in 400 of water, and pour in a solution of 2 parts of aniline nitrite and 2 of phenol in 200 of water. The solution soon becomes turbid and deposits the azo-compound, which should be collected after 24 hours, dissolved in dilute ammonia to separate resin, and the filtered solution precipitated with hydrochloric acid. After recrystallisation from boiling dilute alcohol the substance melts at 148—154°.

*Paramethylhydroxybenzene* or *Paracresoldiazobenzene*,



may be prepared in a similar manner, substituting pure paracresol for phenol. The product is purified from an oily substance by repeated crystallisation from boiling alcohol. It forms lustrous red crystals (m. p. 108—109°) which are but little soluble in cold and only moderately soluble in hot alcohol. It is soluble in ether, in alcohol, and in alkaline solutions. C. E. G.

**Cymenecarboxylic Acid.** By E. PATERNO and P. SPICA (*Gazzetta*, 9, 400).—It has been shown (*Gaz.*, 5, 30) that when sodium cymenesulphate is distilled with potassium cyanide, an oil is produced which may be converted into the amide  $C_6H_3Me(C_6H_7).CONH_2$  (m. p. 138—139°) by the action of alcoholic potash. Although this compound resists the action of alcoholic potash in a remarkable degree, it splits up when fused with potash, yielding an acid of the formula  $C_6H_3Me(C_6H_7).COOH$ , crystallising in slender needles (m. p. 63°) and isomeric with Rossi's homocuminic acid (m. p. 52°). The amide is converted into the acid much more readily by heating it with concentrated hydrochloric acid at 180° than by fusion with potash. The authors have endeavoured to prepare cymenecarboxylic acid by other methods, such as fusing the cymenesulphate with sodium formate, and by the action of sodium and carbonic anhydride on bromocymene, but without any satisfactory result. C. E. G.

**Metamidocinnamic Acid.** By G. MAZZARA (*Gazzetta*, 9, 425—428).—The metanitrocinnamic acid from which the amido-acid was obtained was prepared according to Schiff's method by heating nitrobenzoic aldehyde with acetic aldehyde and sodium acetate. On reducing the nitro-group in the acid by boiling it with tin and hydrochloric acid, and subsequently removing the tin by means of hydrogen sulphide, the *metamidocinnamic acid hydrochloride*,



was obtained in thin plates, permanent in the air and soluble in hot alcohol, from which it crystallises in needles. The amido-acid separated from the copper salt by hydrogen sulphide was very unstable.

Attempts were made to oxidise the amido-acid with nitrous acid, so as to obtain the corresponding metahydroxycinnamic acid, which with cumaric and paracumaric acids would complete the series of the three possible hydroxycinnamic acids. It was found, however, that the action went much further, metahydroxybenzoic acid,  $C_6H_4(OH)COOH$  (m. p. 196—197°) being produced. C. E. G.

**Synthesis of Phenylcoumarin.** By A. OGIALORO (*Gazzetta*, 9, 428—432).—On heating 20 parts of salicylaldehyde with 28 of dry sodium alaphatolate and 70 of acetic anhydride at 150° for 8 hours, a red-brown crystalline mass is obtained which is boiled with water for some time and then allowed to cool. The insoluble portion, when treated with a hot solution of sodium carbonate, partly dissolves, and on acidifying the liquid, *acetylphenylcoumaric acid*,  $C_{17}H_{14}O_4$ , is precipitated in the crystalline state. The portion remaining undissolved, which is the chief product of the reaction, is impure phenylcoumarin.

Acetylphenylcoumaric acid, when purified by crystallisation from boiling water, in which it is moderately soluble, forms long, white, very slender needles. It is soluble in alcohol and in ether, but only sparingly so in cold water. When heated, it begins to soften and give off gas at 170°, but at 180° it fuses to a transparent liquid; if after being allowed to cool it is again heated, it melts at 130°. From this the author is inclined to believe that when the acid is heated, it loses acetic acid and is converted into phenylcoumarin. The *silver acetylphenylcoumarate*,  $C_{17}H_{14}O_4Ag$ , obtained by precipitating the sodium salt with silver nitrate, crystallises from boiling water in tufts of slender, colourless needles, which become yellowish-red on keeping.

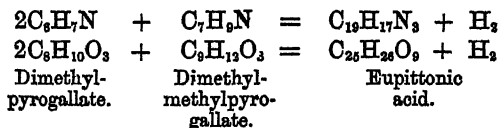
The *phenylcoumarin*,  $C_{16}H_{10}O_2$ , after purification by crystallisation from boiling alcohol, with addition of animal charcoal, forms large transparent colourless prisms (m. p. 139—140°), soluble in ether. It is odourless. Like coumarin, it dissolves when boiled with potash solution, and is precipitated unchanged on adding an acid. When treated with sodium-amalgam in dilute alcoholic solution, phenylcoumarin is converted into a new acid, which may be isolated by acidulating the solution and agitating it with ether. It crystallises in prisms (m. p. 120°), and is, perhaps, phenylmelilotic acid, but has not as yet been further examined.

From its mode of formation the author believes that acetylphenylcoumaric acid has the rational formula  $AcO.C_6H_4.CH : OPh.COOH$ , whilst phenylcoumarin, if regarded as the anhydride of phenylcoumaric

acid, would be 
$$\begin{array}{c} O \\ \diagup \quad \diagdown \\ C_6H_4.CH \\ \quad \quad \parallel \\ CO \quad .OPh \end{array}$$

C. E. G.

**Pittical and Eupittonic Acid.** By A. W. HOFMANN (*Ber.* 12, 2216—2222).—The formation of eupittonic acid is analogous to that of pararosaniline, as is shown by the following equations:—



The sodium and barium salts of this acid have the composition  $\text{C}_{25}\text{H}_{24}\text{Na}_2\text{O}_9$  and  $\text{C}_{25}\text{H}_{24}\text{BaO}_9$ , respectively. The diacetyl derivative,  $\text{C}_{25}\text{H}_{24}\text{Ac}_2\text{O}_9$ , is best prepared by the action of acetic anhydride on an alcoholic solution of sodium eupittonate; it crystallises in yellow needles, which melt at  $265^\circ$  and decompose with evolution of violet vapours. The crystals are soluble in alcohol and are decomposed by alkalis and by acids.

The yellow amorphous substance (*Ber.*, 12, 1371) obtained as a by-product in the preparation of diacetyleupittonic acid by heating a mixture of acetic anhydride and eupittonic acid is insoluble in water, but dissolves freely in alcohol, ether, and acetic acid. It is also dissolved by alkalis and by strong sulphuric acid; on neutralising the alkaline, or diluting the acid solutions, the original substance is reprecipitated.

*Dibenzoyleupittonic acid*,  $\text{C}_{25}\text{H}_{24}\text{Bz}_2\text{O}_9$ , remains as a yellow powder when a mixture of benzoic anhydride and sodium eupittonate is fused and the product extracted with alcohol. The compound dissolves in chloroform, and may be obtained in golden needles (m. p.  $232^\circ$ ) by adding alcohol to the chloroform solution. By the action of benzoic chloride on eupittonic acid, a white crystalline powder is obtained.

*Methyl eupittonate* prepared by the action of methyl iodide on sodium eupittonate is deposited from alcohol in golden needles (m. p.  $242^\circ$ ). The ethyl salt (m. p.  $202^\circ$ ) resembles the preceding compound in its mode of preparation and in its properties.

When a concentrated alcoholic solution of iodine is added to a cold acetic acid solution of eupittonic acid, brown glistening prisms are deposited which have the composition  $\text{C}_{25}\text{H}_{26}\text{O}_9\text{I}_4$ . This compound is decomposed by heat. By the action of strong alkalis and acids, eupittonic acid is regenerated. On treating an alcoholic solution of the iodine-compound with sulphurous acid, hydriodic, sulphuric, and eupittonic acids are formed, but on heating the liquid, the original substance is again formed, since the sulphurous acid decomposes the hydriodic acid with formation of iodine, which at once combines with the eupittonic acid.

Eupittonic acid is decomposed by the action of water at  $270^\circ$ , with formation of dimethyl pyrogallate and a crystalline body which is soluble in alcohol, ammonia, and soda. The dimethyl ether of methyl pyrogallol is not produced by this reaction. Eupittonic triamine undergoes no change on boiling with aniline. When heated at  $250^\circ$  with water, it splits up into ammonia and eupittonic acid.

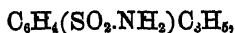
W. C. W.

**Hydroxylation by Direct Oxidation.** By R. MEYER and A. BAUR (*Ber.*, 12, 2238—2241).—The following experiments support the hypothesis that it is only atoms of hydrogen occupying a tertiary position which are capable of undergoing direct oxidation to hydroxyl:—



Normal propylbenzenesulphonic acid is oxidised to carbonic anhydride and potassium sulphate by the action of potassium permanganate in an aniline solution, whilst, under similar conditions, cumenesulphonic acid is converted into hydroxypropylbenzenesulphonic acid,  $C_6H_4(SO_3H)C_3H_6OH$ .

By treating the product of the action of phosphorus pentachloride on this acid with ammonia, propenylbenzenesulphamide,



is formed. This sulphamide melts at  $152^\circ$ , and combines readily with bromine. W. C. W.

**Cumenesulphonic Acids and a New Cumol.** By P. SPICA (*Gazzetta*, 9, 433—444).—All observers who have hitherto studied the action of sulphuric acid on cumene are agreed that only one sulphonic acid is formed; although there is great discrepancy in the description of the salts which this acid forms, and especially with regard to the amount of water of crystallisation they contain. As, however, it has been shown by Paternò and Spica (*Gaz.*, 7, 21, and this Journal, 1877, 1, 707) that normal propylbenzene forms two sulphonic acids, and analogous results have been obtained with butylbenzene, &c., it seemed highly improbable that cumene (isopropylbenzene) should give such a different result, especially as the author had observed, in the preparation of cumol from the crude cumenesulphate, that a small portion of the product passed over below  $220^\circ$ , and that this did not completely solidify at a low temperature.

The cumene employed in the research was prepared by distilling cumic acid with lime and iron filings and rectifying over sodium. The pure cumene, boiling at  $150$ — $155^\circ$ , was converted into the sulphonic acid by agitating it with twice its weight of a mixture of equal parts of ordinary and of fuming sulphuric acid, the action being completed by heating it at  $100^\circ$  for a few minutes. The sulphonic acid was diluted, neutralised with pure barium carbonate, and the product submitted to a careful fractional crystallisation. By this means the author succeeded in isolating two barium cumenesulphates; the one which is formed in larger quantity crystallises in micaceous scales, somewhat unctuous to the touch, and containing 1 mol.  $H_2O$ , thus confirming the observations of Fittig, Schaeffer, and Koenig; the other, formed only in small quantity, remains in the mother-liquors from the crystallisation of the first salt, being much more soluble. It crystallises in microscopic nodules, and contains  $3H_2O$  or  $3\frac{1}{2}H_2O$ , which cannot be driven off completely without decomposing the salt. The corresponding lead salts are very similar, containing 1 mol.  $H_2O$  and 3 mols.  $H_2O$  respectively. By treating the sodium salts with phosphorus pentachloride and converting the chlorides thus formed into the amides by the action of alcoholic ammonia, two sulphamides are obtained corresponding with the two barium cumenesulphates. The one from the less soluble barium salt is a solid substance which, by crystallisation from dilute alcohol, may be separated into two definite compounds, both containing sulphur and nitrogen, and having the formula  $C_6H_4(C_3H_5).SO_2NH_2$ . The less soluble compound which occurs

in largest quantity forms white micaceous scales (m. p.  $107^{\circ}$ ), very soluble in alcohol, soluble also in boiling sodium carbonate solution without alteration; the more soluble compound obtained from the mother-liquors of the first is relatively small in quantity and crystallises in white scales (m. p.  $96^{\circ}$ ). The sulphamide corresponding with the barium salt with  $3\text{H}_2\text{O}$  is a brown oily liquid which could not be purified, but the author believes it to be identical with the crystalline sulphamide mentioned above as melting at  $96^{\circ}$ . The sulphamide (m. p.  $107^{\circ}$ ), when oxidised by fusion with potash, appears to yield a mixture of salicylic and parahydroxybenzoic acids, whilst the oily sulphamide gives a small quantity of a very impure acid, melting between  $150^{\circ}$  and  $170^{\circ}$ .

*Cumol*,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\cdot\text{OH}$ .—The crystallisable cumol (m. p.  $61^{\circ}$ ) obtained from the cumenesulphonic acid formed in largest quantity has already been described by Paternò and the author. The small quantity of the sodium salt of the second sulphonic acid at the author's disposal yielded about 5 grams of a new phenol by fusion with potash in the ordinary way. This new cumol is an almost colourless liquid, and boils at  $218\cdot5^{\circ}$  (cor.) under a pressure of  $756\cdot18$  mm. It does not solidify when cooled with ice and salt. It is slightly soluble in water, and the solution is coloured violet by ferric salts.

In order to ascertain the constitution of the two cumols, they were converted into the corresponding ethyl ethers in the usual way and then oxidised with chromic mixture. The *ethylcumol*,  $\text{C}_9\text{H}_{11}\cdot\text{OEt}$ , from the solid cumol (m. p.  $61^{\circ}$ ) is a colourless, mobile liquid (b. p.  $220^{\circ}$  cor. at  $757$  mm.) and sp. gr. at  $0^{\circ} = 0\cdot94377$ , at  $100^{\circ} = 0\cdot86369$ . By oxidation it yields paraethoxybenzoic acid (m. p.  $194\text{--}195^{\circ}$ ). The *ethylcumol* from the liquid cumol boils at  $213^{\circ}$  (uncor.), and on oxidation gives an oily acid soluble in alcohol and in ether, besides a small quantity of an acid melting at  $194^{\circ}$ . Ethylsalicylic acid melts at  $19\cdot5^{\circ}$  C. From these results it would seem that the solid cumol is *para*isopropylphenol, and the liquid cumol *ortho*isopropylphenol. It is evident also that the perfect separation of the isomeric barium cumenesulphonates cannot be effected without great difficulty.

C. E. G.

**Empirical Formula of Skatole.** By M. NENCKI (*J. pr. Chem.*, **20**, 466—469).—This product is the result of long putrefaction of animal matter, and its formation is subsequent to that of indole and phenol. The author prepared it by the putrefaction of pancreas and muscle for five months. The putrefied mass was acidified with acetic acid and distilled, and the skatole, which volatilised with water-vapour, was separated from the distillate by acidifying it with hydrochloric acid and adding picric acid. On analysis, it gave numbers agreeing with the formula  $\text{C}_9\text{H}_7\text{N}$ , and its picric derivative has the formula  $\text{C}_9\text{H}_5\text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{OH}$ . The author throws out the suggestion that skatole is methylindole.

W. R.

**Action of Chlorine on Naphthalene- $\alpha$ -sulphonic Chloride:**  
 $\gamma$ -Trichloronaphthalene. By O. WIDMANN (*Ber.*, **12**, 2228—2231).—The tetrachloride of the  $\alpha$ -sulphonic chloride,  $(\text{C}_{10}\text{H}_6\text{Cl}_4\text{SO}_2\text{Cl})\text{Cl}_4$ , formed

when chlorine (2 mols.) is passed into a solution of naphthalene- $\alpha$ -sulphonic chloride in carbon bisulphide: it is an oily liquid, freely soluble in the usual solvents: it has not yet been solidified. The potassium dichlorosulphonate, which is obtained by the action of alcoholic potash on the tetrachloride, yields on treatment with phosphorus pentachloride, *dichloronaphthalene- $\alpha$ -sulphonic chloride*,  $C_{10}H_7Cl_2SO_2Cl$ . After recrystallisation from boiling glacial acetic acid and from benzene, the chloride is deposited in glistening needles or scales (m. p.  $145^\circ$ ). Heated in sealed tubes with water, it yields dichloronaphthalene- $\alpha$ -sulphonic acid.  $\gamma$ -*Trichloronaphthalene*,  $C_{10}H_5Cl_3$ , previously described by Atterberg (*Ber.*, 9, 316), is formed when the sulphonic chloride is distilled with phosphorus pentachloride. This derivative yields dinitrodichlorophthalic acid on nitration, which indicates that the  $\gamma$ -trichloronaphthalene contains two chlorine atoms in one benzene nucleus and one chlorine atom in the other. Hence it is probable that the only difference in the constitution between the  $\gamma$  and  $\zeta$  compounds is that the isolated chlorine atom occupies the  $\alpha$  position in the one compound and the  $\beta$  position in the other. W. C. W.

**Dichloronaphthalene- $\alpha$ -sulphonic Acid.** By O. WIDMANN (*Ber.*, 12, 2231—2233).—This acid,  $C_{10}H_7Cl_2SO_3H$ , is deposited in colourless needles when dichloronaphthalene- $\alpha$ -sulphonic chloride is heated with water at  $140^\circ$ .

Its salts are crystalline and sparingly soluble in water. They lose a portion of their water of crystallisation at the ordinary temperature, but, to remove the whole, they must be heated nearly to  $200^\circ$ .

$C_{10}H_7Cl_2SO_3K + 2H_2O$  forms needle-shaped crystals. The anhydrous salt dissolves in 115 parts of water at  $15^\circ$ .  $C_{10}H_7Cl_2SO_3Na + H_2O$  crystallises in prisms, and  $C_{10}H_7Cl_2SO_3Ag + 2H_2O$  in silky needles. The barium salt also forms needles which require 1650 parts of water for complete solution. The lead salt (needles) dissolves in 700 parts of water.  $(C_{10}H_7Cl_2SO_3)_2Ca + 4H_2O$  crystallises in quadratic plates, 1 part of the salt dried at  $100^\circ$  dissolves in 1270 parts of water at  $14^\circ$ , and in 145 at  $100^\circ$ . The zinc salt forms pearly scales containing 7 mols. of  $H_2O$ .

The amide,  $C_{10}H_7Cl_2SO_2NH_2$ , forms feathery crystals soluble in water and alcohol, which melt and blacken at  $250^\circ$ . W. C. W.

**Phenylnaphthylcarbazon.** By C. GRABBE and W. KNECHT (*Ber.*, 12, 2242—2243).—The carbazon,  $C_{18}H_{11}N$ , discovered by Brunck (*Ber.*, 12, 341) in crude anthracene, is formed synthetically when  $\beta$ -phenylnaphthylamine is passed through a red-hot tube. W. C. W.

**Balsamum Antarthriticum Indicum.** By B. HIRSON (*Arch. Pharm.* [3], 15, 27—47).—Three specimens, labelled *Balsamum antarthriticum Indicum*, Wapa balsam, and oil of Wapa, together with a block of wood of the same sort as that from which the above were prepared, *Euperna falcata*, came under the author's observations. He concludes from careful comparison that the balsams and oil closely resemble one another in their chemical and physical properties, but

that the wood in its present state (being without bark or centre) could not, without the addition of other materials produce the balsam.

E. W. P.

**Coca.** By G. W. KENNEDY (*Pharm. J. Trans.* [3], 10, 65).—The physiological action of coca in small doses is to produce excitement of the functions, to relieve or prevent muscular fatigue, and, to some extent, to take the place of food; large and frequent doses produce effects similar to those of opium. Attempts have been made to isolate the narcotic principle which produces these effects. Neumann discovered an alkaloid named *cocaine*; a volatile alkaloid, *hygrine*, has also been separated, and an essential oil which imparts the peculiar odour to the leaves. Cocaine or erythroxyline appears to be the active principle; it is soluble in 704 parts of water, more soluble in cold alcohol, and quite soluble in hot alcohol and ether. The author gives proportions and directions for the preparation of a fluid alcoholic extract, and an elixir.

F. C.

**Berberine Salts.** By J. U. LLOYD (*Pharm. J. Trans.* [3], 10, 125—127).—The finely powdered roots of *Hydrastis canadensis* are extracted with alcohol by percolation; the extract is cooled by ice, and mixed with excess of sulphuric acid; and after it has been kept cool for about twelve hours the precipitate is separated by filtration and stirred up with cold alcohol; and the impure berberine sulphate is separated and dried by exposure to the air.

*Sulphate of berberine* in the pure state is obtained by adding the above impure product to 16 parts of water, dropping in ammonia in slight excess, with constant stirring, and allowing the liquid to stand in a cool place for twelve to twenty-four hours. The liquid is then filtered, cooled by ice, and exactly neutralised with sulphuric acid: the crystals can be strained off in a few hours. The sulphate is orange-red, soluble in about 100 parts of water at 21° C.; it is readily decomposed by alkalis, yielding free berberine. It is unaffected by exposure to the air, but becomes moist if extractive matter or sulphuric acid is present. From 18 to 20 ounces are obtained from 100 pounds of *hydrastis*.

The author prepares pure *berberine* from the sulphate by treating it with slight excess of ammonia, dissolving in alcohol, and precipitation with ether. Berberine is soluble in about  $4\frac{1}{2}$  parts of water at 21°, moderately soluble in alcohol, and insoluble in ether and chloroform. It readily yields salts with acids: the pyrophosphate is very soluble, the picrate insoluble in water. The phosphate, hypophosphite, and chloride are readily prepared by adding the respective acids in slight excess to an aqueous solution of berberine. The ortho-phosphate is soluble in 280, and the hypophosphite in about 60 parts of water.

*Berberine hydrochloride*, prepared by precipitation, is soluble in about 500 parts of water; almost insoluble in cold alcohol, ether, and chloroform.

*Berberine nitrate* is greenish-yellow, it is made in a similar way to the chloride, and resembles it closely in solubility.

*Remarks.*—The alcoholic extract of *Hydrastis canadensis* contains,

besides berberine, a greenish fixed oil, an acrid resin, a white alkaloid, a vegetable acid, yellow colouring matter, and small amounts of other substances. These substances are probably combined in the root, but on adding an acid, the alkaloids are converted into sulphates, with separation of the vegetable acid, the resinous matters and the colouring matter. In the process given above for preparing berberine, the impure berberine sulphate is decomposed by ammonia, a slight excess of which precipitates the white alkaloid *hydrastine*, together with the resin and oil. The berberine sulphate made from the filtrate by cooling and adding sulphuric acid, contains some ammonium sulphate and foreign matters; it may be purified by dissolving in hot alcohol and recrystallising.

The volatile oil is obtained by distilling the root with water. When the mother-liquor of the berberine sulphate crystals is mixed with its own bulk of water, and the alcohol removed by evaporation, the green fixed oil rises to the surface, and the resinous substances settle to the bottom. The water contains the hydrastine as sulphate. Hydrastine is separated from this solution of its sulphate by adding ammonia in excess in the cold; it is purified by converting it once more into sulphate, reprecipitating with ammonia, and crystallising from boiling alcohol. The crystals are coloured yellow by admixture with a yellow substance; they are not bitter, but acrid; hydrastine is almost insoluble in water, somewhat soluble in cold alcohol, and freely soluble in boiling alcohol and in chloroform: it forms salts with acids, which are, as a rule, very soluble and difficult to crystallise. F. C.

**Veratrum viride.** By C. BULLOCK (*Pharm. J. Trans.* [3], 10, 186).—The powdered rhizome and rootlets of this plant were exhausted with alcohol, and after evaporation, the residue was freed from alcohol by a continued moderate heat: the resin which separated from the soft extract was removed and allowed to drain for several weeks during warm weather.

*The Soft Extract.*—86 per cent. was soluble in water; 43 per cent. of fatty matter was removed by light petroleum. The aqueous extract was concentrated and made alkaline with sodium carbonate: after filtering off the precipitated alkaloids, the solution was heated to 66° C. and a little soda added; the additional precipitate was then filtered off while the liquid was warm: the precipitated alkaloids from 1 pound of root amounted to 19.3 grains, about one-ninth of which was precipitated by warming after addition of soda. Colouring matter was removed by dissolving in acetic acid and reprecipitating from the warm solution: and the united mother-liquors, after being acidified and evaporated, were made alkaline, treated with ether, the ether product dissolved in acetic acid, filtered, and precipitated as before. The total weight of mixed alkaloids obtained was 12.4 grains, of which 1.7 grains had been separated from the mother-liquors.

The *jervine* was precipitated as nitrate from an acetic acid solution containing 3 grains in each fluid ounce, by addition of an equal volume of saturated potassium nitrate solution. The precipitate was filtered off after six hours, washed with potassium nitrate solution, pressed between bibulous paper, and dried: its weight was 7.9 grains, and the

weight of alkaloids precipitated from the concentrated filtrate by warming with soda was 3·2 grains.

The aqueous solution, after removal of the alkaloids, was treated with subacetate of lead, the excess of lead separated, and the free acid neutralised with barium carbonate; the filtered solution was then evaporated to a syrup, and thrown into alcohol. The filtered alcohol solution, evaporated and dried at 100°, yielded a product with sweet and somewhat bitter taste, energetically reducing copper and silver salts, and apparently consisting almost entirely of glucose: its weight amounted to 8·5 per cent. of the total aqueous extract.

The alkaloids were then removed from the resin, both that from the soft extract and also the hard resin. Fatty matter was first dissolved away by light petroleum, then the powdered resin was made into a smooth paste with water, and dissolved in a solution of sodium carbonate containing soda. The alkaline solution was twice agitated with ether, and the ether extract dissolved in acetic acid, filtered, and the alkaloids precipitated as above; the alkaloids were also extracted from the mother-liquor, and the jervine separated from the alkaloids as nitrate. A further minute quantity of alkaloids was obtained from the alkaline solution of the resin.

The total amount of alkaloids obtained from the extract representing 1 pound of root was 46·6 grains, and from this, 31·2 grains of nitrate of jervine and 11 grains of other alkaloids were obtained, the loss of 10 per cent. representing loss and removal of foreign matter. About one-quarter of the total weight of nitrate of jervine was obtained from the soft extract and from the resin from the soft extract, the hard resin yielding about one-half of the total weight. Wright obtained only 0·80 gram of alkaloids per kilogramme of the root employed; the author obtains 6·612 grams: the excess being due probably to the alkaloid separated from the resin by the author.

The alkaloids, after separation of the jervine and crystallisation from alcohol, showed under the microscope crystalline forms differing from jervine, the substance probably being Wright's pseudojervine: when purified, it amounted to 5 per cent. of the mixed alkaloids.

*Saponification of the Haril Resin by Lime.*—From 1 pound of the hard resin the fatty matter was removed by light petroleum; it was then rubbed into a smooth paste with 2 pounds of slaked lime, water added, and the mixture boiled for a few minutes. After evaporation and drying on the steam-bath, the powdered mass was exhausted with 3 gallons of hot alcohol. The alkaloids obtained from the alcoholic extract, when purified by reprecipitation, amounted to more than 485 grains, a quantity 20 per cent. greater than that yielded by the ether process, and corresponding to 4·21 grams per kilogram of the root.

F. C.

**On Casein, and the Action of Rennet.** By O. HAMMARSTEN (*Bied. Centr.*, 1879, 147).—Pure casein may be prepared by precipitating with acetic acid, care being taken to avoid excess of acid, dissolving the washed precipitate in alkali, so that the solution remains slightly acid, filtering from separated fats, reprecipitating several times by acetic acid, and washing with alcohol and ether. The casein thus

prepared appears to be a weak acid, dissolving calcium and barium carbonates, and calcium phosphate. Salts appear to keep casein in solution, and this accounts for the fact that, in the precipitation of casein by acids, the amount obtained is not equivalent to the acid employed. Rennet, when it precipitates casein, appears to break it up into two albuminoids, one which is greatest in quantity is combined with calcium phosphate, and appears as cheese; the other (a peptone) remaining dissolved in the whey. For complete precipitation, the presence of calcium phosphate is necessary, and this accounts for the fact that dilute milk cannot be coagulated. The presence of calcium chloride also partly aids curdling, and one part of rennet ferment is capable of curdling 800,000 parts of casein. E. W. P.

**Fibrinogen.** By O. HAMMARSTEN (*Pflüger's Arch. f. Phys.*, 19, 563—622).—The author's researches have led him to regard paraglobulin and fibrinogen as entirely distinct substances, each characterised by well-marked properties. In the present communication, he describes his method for preparing fibrinogen from venous blood, and claims for the substance so prepared that it is perfectly free from hæmoglobin, serum, albumin, and paraglobulin, that it is in no way altered by the process of preparation, and that it is the true parent body whence fibrin is derived.

To prepare fibrinogen, the author mixes 3 vols. of blood with 1 vol. of a saturated solution of magnesium sulphate, filters, and precipitates by addition of an equal volume of a saturated solution of sodium chloride. After continued shaking, the precipitated fibrinogen is removed, broken in very small pieces, and shaken up with a half-saturated sodium chloride solution. This process of washing with sodium chloride solution is repeated five or six times, care being taken that no lumps are allowed to form in the fibrinogen. The fibrinogen is finally collected on filters, strongly pressed, dissolved in water, and the solution is filtered.

Slight modifications of this method are described, and the process is compared, at great length, with those of Gautier and A. Schmidt.

The properties of pure fibrinogen are scarcely mentioned in the present paper, but are reserved for a further communication. The author states that a solution of fibrinogen is altered by long-continued dialysis; that it may be frozen without inducing any turbidity, but that if a trace of altered fibrinogen is present, small solid particles separate when the mass is melted; that fibrinogen readily undergoes fermentative changes; and that when precipitated by sodium chloride and allowed to remain in contact with the supernatant liquid, its solubility diminishes. M. M. P. M.

**Note on Hyraceum.** By W. H. GREENE and A. J. PARKER (*Pharm. J. Trans.* [8], 10, 188).—Hyraceum is believed to be the inspissated urine of the Cape Hyrax (*Hyrax capensis*), the urine collecting in hollows of rocks and gradually evaporating; its medicinal effect is reported to be the same as that of castoreum. It is a dark-brown, brittle, resinous substance, with aromatic odour and bitter taste. About 56 per cent. of it is soluble in water, and nearly one-

third of the residue (14 per cent.) in alcohol, ether, and chloroform; of the 30 per cent. of insoluble matter, 14 is woody fibre and insoluble organic material, and 16 consists of sand and other inorganic substances. On ignition, hyraceum leaves 34 per cent. of ash, consisting of chlorides, sulphates, phosphates, and carbonates of sodium, potassium, calcium, and magnesium. Small quantities of nitrates are also present.

When the organic matter in the aqueous extract was precipitated by lead acetate, and the precipitate was decomposed by sulphuric acid, a hard, horny, resinous, brown, transparent substance, emitting a faecal odour, was obtained.

Hyraceum consists of various salts and organic substances; the latter constitute about one-half, and contain urea in small quantity, besides uric, hippuric, and benzoic acids; probably also glyocol, derived from the breaking up of the hippuric acid. Hyraceum is, therefore, undoubtedly derived from a urine; but the large amount of calcium salts in proportion to the other salts, and the character of the organic matter, indicate the presence also of faecal matter.

F. C.

## Physiological Chemistry.

**Assimilation of Ordinary Horse Fodder.** By E. v. WOLFF and Others (*Bied. Centr.*, 1879, 663—667).—After a series of experiments given in detail, it was found that, generally speaking, the various component parts of ordinary fodder were digested as well by horses as by sheep.

J. K. C.

**Fattening of Animals.** By E. v. WOLFF (*Bied. Centr.*, 1879, 661—663).—The author makes some observations on the results given in a paper by Henneberg and others on the fattening of sheep (this Journal, 36, 811), showing by a comparison of the food given and the resulting increase of fat, that at least one-third of this arose from the absorption and assimilation of the carbohydrates contained in the fodder used.

J. K. C.

**Source of Hippuric Acid in the Urine of Herbivora.** By O. LOEW (*J. pr. Chem.*, 20, 476—479).—The author discovered an acid in meadow hay closely resembling quinic acid, but was not successful in demonstrating the identity of the two. On repeating his experiments, he found it impossible to effect a satisfactory separation from a substance resembling peptone; but the impure substance resembles quinic acid by giving hydroquinone with lead peroxide, and proto-catechuic acid with bromine. Researches by several chemists have shown that hippuric acid is not increased in the urine of an animal by giving it quinic acid in its food; and hay, after treatment with soda, is still a source of hippuric acid in urine. But after treatment with sulphuric acid, the source of hippuric acid is removed from hay.



The only definite compound which the author was able to isolate from an extract of hay made with dilute sulphuric acid was some acid resembling quinic acid.

It has been suggested by Weiske that the real source of hippuric acid may be the meadow plants with which hay is mixed. The author, therefore, investigated the officinal extract of dandelion, and again found the acid resembling quinic acid along with some succinic acid, and an acid oil, heavier than water, which gradually became resinous.

W. R.

**Analysis of a Calculus from a Horse.** By P. PETERS and K. MÜLLER (*Bied. Centr.*, 1879, 714).—A calculus formed in concentric layers and weighing 84 kilos, was analysed by the authors with the following results:—

| Water. | Organic matter. | Magnesium ammonium phosphate. | Ferric phosphate. | Calcium phosphate. | Silica. | Soda and potash salts. |
|--------|-----------------|-------------------------------|-------------------|--------------------|---------|------------------------|
| 4.22   | 6.20            | 87.37                         | 0.29              | 0.11               | 1.36    | 0.45                   |

J. K. C.

**Physiological Influence of Adulterated Wine.** By A. SCHMIDT (*Bied. Centr.*, 1879, 712—713).—The unfermentable residues of grape-sugar, which are used for the adulteration of wine, were subjected to experiment with reference to their physiological action. Subcutaneous injection in the case of dogs was found to produce vomiting and general derangement. The author is of the opinion that these residues contain a poison similar to that in fusel oil.

J. K. C.

**Chemical Cause of the Toxicological Action of Arsenic.** By C. BINZ and H. SCHULZ (*Ber.*, 12, 2199—2202).—The authors are of opinion that arsenic owes its poisonous nature to the alternate oxidation of arsenious to arsenic oxide and reduction of arsenic to arsenious oxide, which produces a rapid oscillation of the atoms of oxygen in the molecules of albumin, causing their complete destruction. Arsenic acts as a carrier of oxygen, resembling nitric oxide in this respect. Phosphorus and the other members of the nitrogen group appear to act in a similar manner. The authors base their opinion on the following observations:—(1.) That in cases of arsenical poisoning, it is those portions of the system which have the power of taking up oxygen from the blood which suffer most severely; (2.) and that egg albumin, blood fibrin, and brain reduce arsenic oxide to arsenious at a blood heat, and that the salivary glands and liver not only reduce arsenic to arsenious oxide, but also oxidise arsenious to arsenic oxide, whereas blood, hæmoglobin, and fat have no action on the oxides of arsenic.

W. C. W.

**Presence of Alcohol in Animal Tissues during Life and after Death.** By J. BÉCHAMP (*Compt. rend.*, 89, 573—574).—In order to verify the truth of the statement that flesh superficially coagulated would rapidly putrefy under conditions in which well-cooked flesh would remain sound for many weeks, some horseflesh was coagulated by immersion for ten minutes in boiling water, then wrapped in

a closely woven cloth, and placed aside for eight days. At the expiration of that time, the meat was found in an advanced state of decomposition, and the muscular striation had disappeared, although the air had not penetrated to the interior of the substance, whilst bacteria and vibrios abounded. By methods described in the original memoir, the author isolated and characterised about 0·8 gram of alcohol and 10 grams of sodium salts formed by acetic, butyric, and other acids. The alcohol was converted into aldehyde, and oxidised to acetic acid, so that its identity was established beyond doubt; within certain limits the quantity obtained was larger, the further the extent of the decomposition.

It would seem, therefore, that the phenomena accompanying putrefaction are very closely allied to those belonging to fermentation properly so called, perhaps more directly with those of the butyric fermentation. By the same process alcohol was obtained from the *fresh* tissues. The brain of sheep gave a larger quantity than the liver, but the largest quantity was obtained from the brain of an ox, which furnished sufficient alcohol to measure with the hydrometer. It may be argued, therefore, that in medico-legal cases, the detection or separation of alcohol from putrid or healthy tissues, is not sufficient evidence to show that alcohol has been administered at all, still less that this liquid has been the cause of death.

J. W.

## Chemistry of Vegetable Physiology and Agriculture.

**Unorganised Ferments in Plants.** By C. KRAUCH (*Bied. Centr.*, 1879, 120—122).—The ferments from various plants were obtained by the method of Wittich, or by that proposed by Erlenmeyer. For the detection of diastatic fermentation, the decomposition of starch into sugar and dextrin was employed. The action of the ferments on albuminoids could be studied only when free acids (2 : 1000) were present; to detect and recognise the ferments which act on fats, the decomposition (1) of an emulsion of gum arabic water; (2) of oil with free acid and glycerol; (3) of oil in the state of an emulsion, were taken advantage of.

The substances which came under examination were buds and twigs of horse chestnut, which were separated into wood and bark; the same also of the birch; the young and old bark and wood of oak, the leaves of hawthorn; bulbs and tubers; starchy grains, as barley and maize, the endosperm and embryo being in the last grain examined separately; oily seeds, as pumpkin. In no case could albuminous or fatty ferments be detected. A strong diastatic ferment is found in the horse chestnut at all periods of growth. Slight fermenting action in the leaves of oak and hawthorn, whilst the birch is free of ferment. In onions and potatoes, a weak ferment is present, but during the period when there is no growth, the onion alone possesses a ferment. Diastase is present in unsprouted barley, but the action is weaker than that of malt

diastase; in unsprouted maize diastase is found only in the embryo and hilum. It would seem, therefore, that in all starch-containing plants, diastase is present more or less, the quantity being dependent on the amount of starch present; but the change of starch into glucose does not necessitate the presence of diastase: for example, the birch contains no diastase at any time. Further experiments were directed towards determining the action of the ferment of the above plants on gum arabic and quince emulsion; in all cases sugar was formed. The ferment of oak and hawthorn leaves, malt and pumpkin seeds, affected salicin, but the action was most energetic in the case of the pumpkin seeds; only oak leaf ferment had any action on amygdalin, and that only after 48 hours' contact. The composition of diastase is given as C, 45.68; H, 6.90; N, 4.57; ash, 6.08; O, 36.77 parts per hundred; sulphur is also present in small quantities. E. W. P.

### Chemical Composition of Bacteria in Putrefying Liquids.

By M. NENCKI and F. SCHAFFER (*J. pr. Chem.*, 20, 443—465).—The authors have found that on adding a few drops of acid (sulphuric, hydrochloric, or acetic) to a liquid containing bacteria, and boiling it for a few minutes, the bacteria shrivel up, and settle; the liquid may then be filtered, and the bacteria separated in a "chemically pure" condition. Of course the fluid must contain no substances precipitable by boiling, such as albumin. Ordinary gelatin was therefore chosen as a suitable medium for propagating the growth of bacteria.

The dried mass of bacteria was first exhausted with alcohol, and the alcoholic extract then treated with ether. A slight brownish residue of a substance resembling peptone was left. The ethereal extract contained the fat, the elementary composition of which—72.54 per cent. C., and 11.73 per cent. H—corresponds fairly with that of vegetable and animal fats, but contains 1.5 per cent. too little carbon.

In order to ascertain whether any change in the composition of bacteria occurs in the course of their development, analyses were made of undeveloped granules, of a mixture of granules and rod-like bodies, and of the rod-like bodies after full growth. The results are as follows:—

|  | Pure granular mass<br>( <i>Zoogloea</i> ). | Granular mass with partially developed bacteria. | Perfect bacteria. |
|--|--|--|-------------------|
| Water .....  | 84.81                                      | 84.26  | 83.42             |
| Fat (contained in dry substance) .....                   | 7.89                                       | 6.41   | 6.04              |
| Ash (in substance deprived of fat) ....                  | 4.56                                       | 3.25   | 5.03              |
| Elementary composition of the substances deprived of fat | C  | 53.07  | 53.82             |
|  | H  | 7.09   | 7.76              |
|  | N  | 13.82  | 14.02             |
|  | a. 14.60                                   |  | a. 13.82          |

An estimation was made of the albuminoid substance contained in

the bacteria, by exhausting the mass with very dilute alkali, separating the soluble from the insoluble portion by filtration, neutralisation with hydrochloric acid, and precipitation by addition of crystals of salt. The precipitate consists of a new albuminoid, soluble in excess of acetic acid, and has been named by the authors *mycoprotem*. It contains 52.32 per cent. C.; 7.55 per cent. H., and 14.75 per cent. N., and corresponds well with the formula  $C_{26}H_{42}N_8O_9$ . It was proved that neither sulphur nor phosphorus were present. Freshly precipitated mycoprotem is easily soluble in water, alkalis, and acids, but after being dried at  $110^\circ$ , it is no longer perfectly soluble in water. It exhibits the usual properties of an albumin, and is laevorotatory,  $[\alpha] = -79$ . Acids convert it into peptones. The authors believe that this simple form of albumin is obtained from a simple organism; a general law may be deduced, the more complex the organism, the more complex its proximate chemical constituents.

The residue left insoluble on treating the bacteria with dilute alkali, consists of cell-membrane, and amounts to about 5 per cent. of their weight; it contains a little nitrogen. This may point to some albumin not removed, for Loew analysed similar cell-membranes, and found them to contain a mere trace, or no nitrogen. W. R.

**Germinating Power of Beetroot Seeds.** By A. PETERMANN (*Bied. Centr.*, 697—699).—The author is of opinion that beetroot seeds of good quality should have a germinating power of not less than 85 per cent.; he also observes that this depends very largely on the ripeness of the seeds at the time of gathering. J. K. C.

**Influence of Smoke on the Development of Blossoms.** By E. DA CANTO (*Bied. Centr.*, 1879, 715).—It is found in the Azores that the entrance of smoke into the conservatories causes a rapid development of the buds in the case of roses, ananas, &c., and this fact is now made use of in hastening the blooming. J. K. C.

**Causes of the Change in the Form of Etiolated Plants.** By E. GODLEWSKI (*Bied. Centr.*, 1879, 715—716).—The author shows that want of light stops the growth of the cotyledons, and favours that of the stems; hence the changes of form observed. J. K. C.

**Notes on Cinchona Bark.** By D. HOWARD (*Pharm. J. Trans.* [3], 10, 181).—The author has been enabled to compare the proportion of quinine and other alkaloids contained in the "natural" bark and in that formed by "renewing," i.e., growing after the artificial removal of the bark. This renewed bark is termed "mossed bark," because the tree, after being stripped of its bark, is usually protected by a covering of moss, whilst fresh bark is being formed. The natural bark was found to be generally inferior to the mossed bark, since it had been collected either from the upper stem, or from inferior old trees, whereas the mossed bark represents the product of the main stems of the oldest trees. As far as the effect of age was concerned, it was found that both the quinine and total crystallisable alkaloid steadily increased in quantity with the age of the trees; this is probably due to

the greater maturity of the trees. The trees from which the bark was taken were specimens of *Cinchona officinalis*. The author, on the other hand, confirms from recent experience an opinion previously expressed, that the bark of *succirubra* deteriorates in quality when the tree has passed a certain age. Root bark shows a marked tendency to develop the dextrogyrate alkaloids. A sample of renewed bark, which had been formed without "mossing," or any kind of protection, was also examined, and was found equal in quality to the best mossed bark; hence it appears that the only advantage of mossing is to enable the tree to form bark again with a minimum injury to its health; the process does not appear to improve the quality of bark formed. The author also compares the proportions of alkaloids contained in outer and inner bark; the outer bark not only contains a larger quantity of alkaloids, but these contain a larger proportion of quinine; hence it has been suggested to shave off only the outer layers, without cutting quite through the bark.

F. C.

**Relation of Yield of Beet to Rain and Sunshine.** By J. HANAMANN (*Bied. Centr.*, 1879, 694—697).—The author has made observations in Bohemia, on the relation of beetroot produce to the weather during the last twelve years, and arrives at the following conclusions. A mean temperature of from 14 to 18° C., from May to October inclusive, and a warm and wet spring, together with a not too dry summer, are the best conditions under which beet can be grown.

J. K. C.

**Researches on the Ripening of Grapes and Fruits.** By C. PORTELE (*Bied. Centr.*, 1879, 123—131).—The composition of apples, pears, and other fruits was determined at various periods of their growth. The results are as follows:—The absolute weight of pears and apples increases, whilst that of grapes increases only up to the time when colour appears, and then begins to decrease. The percentage of dry matter in the pear at first increases and then diminishes, whereas with apples the decrease is sudden and then remains constant. In the same way alteration of the amount of insoluble residue occurs. The percentage of ash constantly sinks, which with the apple is twice as great as with the pear. The amount of free acid is greatest in the young pear, gradually sinking, but again slightly increasing at the end of ripening; this last does not occur in the apple. Grapes differ from kernel fruit in that with them there is not only a change in the relative percentage of the various acids present, but also a decided decrease in the total free acid. Pears appear to contain at first only tannic acid, which gives place to malic acid as growth proceeds, whilst the apple appears to contain both, and these diminish regularly. Sugar increases as apples, pears, and grapes ripen, but with grapes it is the dextrose which increases most, whilst lævulose increases in greatest proportion in other fruits.

Comparing the constitution of the leaves with the fruit, we find that the acid in the leaf is present in greatest quantity when that in the fruit is lowest. Sugar increases in the leaf and then decreases, and there is more present in the leaf at first than in the fruit; lævulose and dextrose are present in equal quantities.

Other specimens of fruit were examined which had been plucked and put aside to ripen, and it was found that the loss in weight was less, the riper the fruit was when plucked. Fibre, &c., and acid decrease, but sugar increases, and dextrose is converted into lævulose.

Various other fruits, as strawberries, peaches, &c., were also examined, and with similar results. E. W. P.

**Depreciation of Barley by Overgrowth.** By LAUENSTEIN (*Bied. Centr.*, 1879, 676—681).—The difference between barley gathered at the right time and barley which has been allowed to lie out on the field for some time after it was ripe is not clearly shown by direct chemical analysis. An examination of the separate constituents is necessary in order to ascertain the changes which have taken place. In carrying out this plan the author turned his attention first to the starch present in the seed. Ordinary barley contains 64 per cent; in the overgrown corn was found, however, only 58 per cent., the remainder having been converted into dextrin and sugar: a loss of 10 per cent, therefore, on the total quantity of starch was discovered. The change which the starch had undergone would of course not affect the nutritive value of the barley; this, however, was not the case with the albumin, nearly one-fourth of which was found to be converted into amido-compounds, which are of very little nutritive value. The worth of barley for the preparation of malt depends to a very large extent on its powers of germinating. This was found to have suffered a loss of 53 per cent. in the overgrown corn.

J. K. C.

**On the Quantities of Acid and Sugar in Grapes cut at Various Stages of their Growth.** By P. WAGNER and W. ROHN (*Bied. Centr.*, 1879, 681—686).—These researches have been so far only of a tentative character, the object being to discover if possible a practicable method of examining various sorts of grapes at different stages of their growth, and chiefly at the ripening stages. The authors carried out their researches at six different places, with vines of various kinds. The grapes were cut four times during the last month of ripening, and the relative quantities of sugar and acid determined in the sap. In some cases the relation improved, in others it remained constant for some weeks. The authors hope, by repeating these observations for some time to come, to arrive at results of great practical value.

J. K. C.

**Ripening of Apples after Gathering.** By F. TSCHAPLOWITZ (*Bied. Centr.*, 1879, 686—689).—The author finds that the loss of weight undergone by apples on keeping is dependent on the position in which they are left and the dryness of the surrounding air. It may be almost entirely considered as loss of moisture, the amount of carbonic anhydride which is given off being but very small. It is noticeable that smaller apples lose more in weight than those of a larger description. The temperature of the fruit is also the same as that of the air.

The results of various analyses show that the quantity of sugar in

the apples increases during the ripening process at the expense of the pectin and acid.

J. K. O.

**Decomposition of Albuminoids in Pumpkin Sprouts.** By E. SCHULZE and J. BARBIERI (*J. pr. Chem.*, 20, 385—418).—The seeds of plants contain albuminoids, starch, and oil, by which the sprouts, which are not able to decompose carbonic anhydride and water, are nourished. During germination the starch and fat decrease, whilst sugar, dextrin, and cellulose are formed, and carbonic anhydride and water are eliminated. From more recent observations, it has also been discovered that the albuminoids become soluble, and that in many plants, especially in Papilionaceae, asparagine is produced. As that body decomposes on boiling with hydrochloric acid into aspartic acid and ammonia, its amount may be determined by estimating the ammonia. Gorup-Besanez afterwards found leucine amongst the decomposition-products of albuminoids. In pumpkin sprouts, which contain no asparagine, Sabania and Laskowski supposed that another amide existed; this was shown to be correct by the authors and by Ulrich. In the beetroot this amide has been shown to be glutamine, and the object of the present paper is to show that it is also present in germinating pumpkin sprouts, along with asparagine, leucine, and tyrosine.

The albuminoids and fatty oil form 86—88 per cent. of the weight of dry pumpkin seeds, the former being present as protein granules. When the crushed seeds are treated with ether, the fat dissolves and the protein substances sink to the bottom of the vessel. They are insoluble in water, but dissolve in a 10 per cent. solution of salt. On addition of solid salt, a small quantity of vegetable myosine separates, and on dilution with water, vegetable vitelline is deposited. Non-albuminoid principles containing nitrogen are present in very small amount in pumpkin seeds.

The sprouts after germination were dried, boiled with alcohol, and the evaporated extract was treated with lead acetate. The filtrate from the lead precipitate was boiled for several hours with hydrochloric acid, and again mixed with lead acetate to remove hydrochloric acid. The filtrate from the lead chloride after evaporation was mixed with alcohol, and the precipitated lead salts were decomposed with sulphuretted hydrogen. The solution filtered from the lead sulphide and treated with silver oxide to remove traces of hydrochloric acid was evaporated, when glutaminic acid,  $C_5H_7NO_4$ , separated in the crystalline state. It was shown that this acid was not present as such in the sprouts, but was formed by the action of hydrochloric acid on glutamine, a body bearing the same relation to glutaminic acid as asparagine does to aspartic acid. From sprouts which had germinated for eight days, 100 grams gave only a few decigrams, but 16 days' growth increased the amount to 1.75 gram of acid, representing 1.74 gram of glutamine. The ammonia produced by the action of hydrochloric acid on glutamine corresponds to twice that amount, and to account for it a search was made for substances which would undergo a similar decomposition with hydrochloric acid. Aspartate of copper, amounting to 0.5 gram in 400 grams, was separated

from the mother-liquors of the glutamic acid, and leucine and tyrosine were isolated by boiling the juice from sprouts 2—3 weeks old; and after precipitating with alcohol and evaporating the filtrate, wart-like crystals were deposited, consisting of tyrosine. From 1,000 grams of fresh sprouts (60 grams when dried), 0.15 gram of tyrosine was obtained, and leucine was isolated from the mother-liquor of the tyrosine, but in much smaller quantity.

The nature of the decomposition products is thus the same as when the albuminoid is heated with baryta-water or hydrochloric acid; but the proportion of each product differs greatly. On decomposing the albuminoids from pumpkin seeds with hydrochloric acid and stannous chloride, 120 grams yielded leucine, 24 grams; tyrosine, 2.5 grams; aspartic acid, 3 grams; glutamic acid, 4 grams; and an uncrystallisable residue of 40 grams, the sum being 75 grams. The difference between 120 and 75 = 45 grams, was lost. If these amounts represent even approximately the proportions in which the nitrogenous materials are present in the mixture, it is seen that they differ greatly from the proportions produced by the decomposition of the albuminoids during germination. The author's explanation is that in a growing plant albuminoids are being formed as well as decomposed, any one of the decomposition products serving as material for their formation. The co-existing decomposition products of albuminoids may, however, not be equally used in the formation of new albuminoids, and those which resist the process of regenerating albumin longest accumulate in largest quantity. Thus leucine, which is produced in large quantity by the artificial decomposition of albumin, is probably one which lends itself best to the natural formation of albumin, and is therefore present in germinating plants in small amount, whilst such substances as asparagine and glutamine are comparatively stable, and resist absorption to form new albuminoids.

In conclusion, the authors remark that as ferments are capable only of changing albuminoids into peptones, some other reason must be sought for to account for their decomposition into much more simple products, and quotes a sentence of v. Nägeli, in which such changes are ascribed to the molecular force of living tissue. W. R.

**The Most Advantageous Method of Sowing Corn.** By F. HABERLANDT (*Bied. Centr.*, 1879, 689—694).—The author has made several experiments with wheat, rye, and barley, with a view of ascertaining the number of seeds per square meter which will give the best yield. His results have necessarily only a special value for the soil and climate in which the experiments were carried out. He was able to obtain a yield twice as great as that usually obtained, and thinks that this might be effected in most cases where the proper conditions are observed. It was noticed that the latest development occurred where the seed was most sparsely sown. J. K. C.

**Proper Thickness and Depth to Sow Corn.** By SCHENK-BAUHOF (*Bied. Centr.*, 1879, 717).

**Amount of Carbonic Anhydride in Shingle.** By G. WOLFF-HÜGEL (*Bied. Centr.*, 1879, 709).—The author brings forward tables



already published in defence of his view that the amount of carbonic anhydride in the ground air is a measure of the degree of impregnation of the soil with organic matter and of the progress of its decomposition.

J. K. C.

**Peaty Soils.** By A. v. SCHWARZ (*Biedl. Centr.*, 1879, 84—93).—The analyses of 26 Austrian peaty soils are given, in which the ash varies from 2.30 to 76.08 per cent. To one soil the author has paid special attention, and he has determined the physical properties (which are here appended) of soil from the moorland of Kirchberg a. W. He also finds that this soil when treated with artificial manures yields average crops. The physical properties of the soil were compared with those of alluvial sand from Rötz, loam, and clay, and are as follows:—

| Soil.      | Weight of 100 c.c. in grams. |            | Sp. gr. water at 17.5 = 1.00. | Contraction and expansion.              |  | Capillary saturation capacity. Saturated with capillary water. |                            |
|------------|------------------------------|------------|-------------------------------|---|--|--|----------------------------|
|            | Air dry.                     | Saturated. |                               | 100 c.c. saturated after drying in c.c. | 100 c.c. dried, when saturated in c.c. | 100 c.c. contain of water                                      | 100 grms. contain of water |
| Peaty .... | 28.7                         | 105.6      | 1.470                         | 39.8                                    | —                                      | 82.0   | 77.6                       |
| Sand ..... | 157.9                        | 190.6      | 2.569                         | 100.0                                   | 100.0                                  | 34.9   | 18.3                       |
| Loam ....  | 155.2                        | 192.9      | 2.729                         | 83.9                                    | 119.2                                  | 43.2   | 22.6                       |
| Clay ..... | 140.1                        | 179.8      | 2.714                         | 70.2                                    | 142.1                                  | 51.5   | 23.6                       |

In the determination of cohesion by Haberlandt's process, clay was found to stand highest and loam lowest, sand naturally possessing none. In the case of adhesion by Schübler's method, clay stands first, then loam, peat, sand.

Masses of soil 10 cm. deep, and exposing a surface of 10 square cm., allowed the passage in 24 hours of 1 c.c. water in the case of peat.

| Soil.       | Hygroscopicity 100 grams dry soil absorb of water | Equal weights specific heat. |                                 |                | Equal volumes saturated with capillary water. |
|-------------|---|------------------------------|---------------------------------|----------------|---|
|             |   | Dried at 100°.               | Saturated with capillary water. | Dried at 100°. |   |
| Peaty ..... | 21.6  | 0.592                        | 0.909                           | 0.110          | 0.960   |
| Sand .....  | 1.1   | 0.209                        | 0.354                           | 0.325          | 0.675   |
| Loam .....  | 3.7   | 0.218                        | 0.396                           | 0.326          | 0.762   |
| Clay .....  | 9.2   | 0.225                        | 0.417                           | 0.289          | 0.804   |

5,760 in the case of sand, 1,674 in the case of loam, and 0·7 in the case of clay.

Conductivity for heat was determined (1) by the increase of temperature of the unheated soils, and (2) by the loss of temperature experienced in cooling. In this the soils were experimented on when dry, and when moist, or saturated with capillary water, the source of heat was 60°, and the original temperature 16·3—16·7°.

From the results, it would appear that under direct action of solar radiation peaty soil when dry assumes a higher temperature than either of the others, but the case is reversed if the soils be moist. As regards the rising of water in columns of sand, loam, and clay, it is found that in 100 days water had risen to the height of 408 mm. in sand, to 1,627 in loam, and to 770 in clay.

E. W. P.

**Composition of Maize.** By L. GRANDEAU (*Bied. Centr.*, 1879, 149).—Analyses of various specimens of maize used as feeding stuffs are given. The best appear to be the Hungarian (nutrient ratio, 1 : 8·8), then American (nutrient ratio = 1 : 8·6), but the American is very hard to crush.

E. W. P.

**New Plant for Fodder.** By J. DEININGER (*Bied. Centr.*, 1879, 700—702).—Seeds of a plant known in India as “gram,” a variety of chick-pea, were planted in various kinds of soil in Hungary. The plant thrived exceedingly well, especially in sandy soils, which were worthless for other purposes, and proved very productive. The following analysis of the seeds show that they are very valuable as fodder:—

|                  | Water. | Protein. | Fat. | Nitrogen-free<br>extract. | Fibre. | Ash. |
|------------------|--------|----------|------|---------------------------|--------|------|
| First year . . . | 10·72  | 12·88    | 4·39 | 58·02                     | 10·20  | 3·79 |
| Second year ..   | 9·80   | 17·68    | 3·77 | 54·32                     | 10·89  | 3·54 |

J. K. C.

**Analysis of Materials used for Fodder.** By P. WITTELSHIEFER (*Bied. Centr.*, 1879, 713).—Analyses were made of soured cabbage leaves, dried sprigs of broom, concentrated residues from a starch manufactory, and potato pulp. The first two proved to be excellent for fodder, but the last was too poor in nutritive matter to be used alone.

J. K. C.

**Feeding Value of some Manufacturers' Waste.** By J. MOSER (*Bied. Centr.*, 1879, 114—117).—The analyses of several feeding-stuffs, which however do not appear in large quantities in the market, are given, and are as follows:—

|   | Album. | Water. | Fat.  | Ether.<br>oil. | Non-<br>nitrog.<br>extract. | Fibre. | Ash. | Sand. |
|---|--------|--------|-------|----------------|-----------------------------|--------|------|-------|
| Fennel seed cake..                                      | 9.23   | 15.28  | 12.0  | 0.15           | 38.12                       | 20.15  | 8.14 | 1.93  |
| Sunflower cake :  |        |        |       |                |                             |        |      |       |
| (1.) As powdery<br>mass.....                            | 10.62  | 38.00  | 6.41  | —              | 28.11                       | 10.48  | 4.96 | 1.39  |
| (2.) As coherent<br>cake.....                           | 8.07   | 37.69  | 23.73 | —              | 19.29                       | 6.05   | 5.10 | 0.62  |
| Pumpkin seed cake.                                      |        |        |       |                |                             |        |      |       |
| Loosely coherent<br>mass.....                           | 11.25  | 32.56  | 25.57 | —              | 9.13                        | 15.68  | 4.79 | 1.02  |
| Decorticated....  | 11.01  | 38.74  | 23.55 | —              | 10.75                       | 10.33  | 5.39 | 0.23  |
| Tobacco seed cake,<br>containing no ni-<br>cotine.....  | 10.69  | 25.60  | 14.60 | —              | 15.08                       | 22.43  | 5.31 | 6.20  |
| Wine lees cake..  | 54.04  | 2.54   | 8.54  | —              | 7.41                        | 11.10  | 1.74 | 9.20  |
| Dried brewers'<br>grains :                              |        |        |       |                |                             |        |      |       |
| Mixed with meal<br>and dried....                        | 12.94  | 18.69  | 6.30  | —              | 38.00                       | 16.95  | 4.31 | 2.81  |
| Fresh and un-<br>dried.....                             | 79.22  | 4.92   | 1.35  | —              | 9.36                        | 3.44   | 0.89 | 0.52  |
| Brandy manufact-<br>urers' waste*,<br>pressed and dried | 12.42  | 24.50  | 11.87 | —              | 39.30                       | 8.78   | 1.52 | 1.61  |
| Suet grievances :                                       |        |        |       |                |                             |        |      |       |
| Boiled and press-<br>ed.....                            | 4.77   | 48.06  | 41.10 | —              | —                           | —      | 4.88 | 0.41  |
| Same not pressed  | 58.29  | 11.75  | 24.20 | —              | —                           | —      | —    | —     |

E. W. P.

**Certain Sorts of Pumpkin.** By C. O. HARZ (*Bied. Centr.*, 1879, 717).—The author recommends *Cucurbita maxima Brasiliensis* and *C. m. elliptica* as the best kinds to grow, because the fruit does not putrefy and can be kept many years. Analysis of the dried fruit gave the following results:—

| Protein. | Fat. | Nitrogen-free<br>extract. | Fibre. | Ash. |
|----------|------|---------------------------|--------|------|
| 10.87    | 1.64 | 72.75                     | 9.39   | 5.35 |

J. K. C.

**Influence of Fodder on the Quantity and Quality of Milk Fat.** By H. WEISKE, M. SCHRODT, and B. DEHMEL (*Bied. Centr.*, 1879, 110—113).—The present opinions concerning the influence of fodder on milk produced are, that dry food produces more solid glycerides in butter than the green feeding of summer, and that a hard butter is produced when the feeding has been scanty, or poor in albuminoid matter. The analyses of the milk of a cow which had been

\* *Note by Abstractor.*—There is evidently a printer's error here, as the above analysis is said to be that of a substance undried, whereas the analysis of the same material which is called "dry," shows a percentage of 61.41 water.

fed at different periods with various kinds of food, show that a high melting point of butter is not dependent on scanty feeding; the melting point, and also the quantity of the butter fats, and of the fatty acids, show no regularity, even when the feeding remains the same. Highly albuminous fodder produces the highest yield of milk; addition of albuminoid matter to fodder increases the amount of fat in milk, but addition of oil and of stearic acid causes a much greater amount of fat and dry substance to be formed. Comparing morning and evening milk, no difference in the amount of solid matter or fat could be detected; and the melting points of the fats were the same on the same days, the melting point of the cream fat being 2° lower than that of the fat of the skimmed milk. The amount of fatty acid insoluble in water varied very considerably, varying from 84—88.9 per cent.

E. W. P.

**Four-yearly Rotation of Crops.** By A. VOELCKER (*Bied. Centr.*, 1879, 658—661).—These experiments were conducted at Woburn on behalf of the English Agricultural Society; the plan of rotation was the following:—1st year, clover; 2nd year, wheat; 3rd year, roots (turnips, &c.); 4th year, barley. The results obtained in 1878 were mostly of a normal character. The author has found that manure obtained after a fodder of cotton seeds is of more value to the land than if the animals had been fed on maize; and that the materials for plant nutriment have a better effect when applied directly to the land than when they have been mixed with fodder and allowed to pass into dung.

J. K. C.

**Manuring of Oats on Fen Lands.** By H. J. CARSTEN (*Bied. Centr.*, 1879, 97—99).—Oats were found to be most prolific on moor land when manured with stable manure.

Comparing the two methods of cultivation, "Veen" and "Damm kultur," it was found that the "Damm" method (covering the moor with a layer of sand), in all cases when the manuring with artificial manures was employed, gave better results than the "Veen" method (where the surface to a depth of 10—12 cm. is mixed with sand).

E. W. P.

**Effect of Gypsum on the Quantity and Quality of Clover Crops.** By A. PASQUALINI (*Bied. Centr.*, 1879, 99).—Clover manured with gypsum is not affected as regards its feeding qualities, although the total yield is increased.

E. W. P.

**Manuring of Sugar Beet.** By J. MOSER (*Bied. Centr.*, 1879, 100—106).—This paper contains an account of the manures used (salts of potash, soda, and magnesia), the yield of roots, tops, and sugar obtained in experiments made in the years 1876—77; but no conclusions are drawn, as the experiments are still being carried on. The manures were employed in quantities equal to one-eighth of the capacity of the soil for potash.

E. W. P.

**Manuring of Beet.** By H. BRIEM (*Bied. Centr.*, 1879, 656—658).—Two kinds of lime manure are used in this investigation, the object

of which was to compare their action. One of these was the ordinary lime-scum from sugar works, and the other a mixture of lime-dust with the residues from a beet and molasses distillery: the latter containing about 43 per cent., and the former 30 per cent. of lime: they were applied to a soil very poor in lime, containing about 4 parts per thousand, the experiments being carried out in two successive years: the mean results are as follow:—

| Manure used.                          | Weight of the beet<br>in grams. |         |       | Polarisation of<br>sap. |        |               | Percentage<br>of |      |
|---------------------------------------|---------------------------------|---------|-------|-------------------------|--------|---------------|------------------|------|
|                                       | Total.                          | Leaves. | Root. | Degrees.                | Sugar. | Not<br>sugar. | Water.           | Ash. |
| None .....                            | 440                             | 105     | 335   | 14·2                    | 10·95  | 3·25          | —                | —    |
| Lime from sugar<br>works.....         | 506                             | 122     | 384   | 15 0                    | 11·67  | 3·23          | 82·8             | 0·80 |
| Lime with distil-<br>lery residues... | 946                             | 210     | 786   | 14·1                    | 9·66   | 4·44          | 84·7             | 0·91 |

The difference in the effects produced by the two manures is very marked: the distillery residues produced a wonderful effect in increasing the total weight of the yield, at the same time, however, deteriorating greatly the quality of the juice obtained, as is observed on comparing the ratio of the quantities of sugar and non-saccharine matter present in the juice: this relation is of the greatest importance to the manufacturer, as a juice containing such a quantity of extraneous matter would be found very difficult to work. J. K. C.

**Influence of Soluble and Insoluble Phosphates as Manure for Turnips.** By T. JAMIESON (*Biol. Centr.*, 1879, 652—656).—These investigations were carried out near Aberdeen, with a view of comparing the effect of phosphoric acid in the soluble and insoluble form applied as manure to turnips. Five fields, lying at considerable distances from one another, were selected, and each made the subject of eighteen experiments, each of which was carried out on two separate plots. The experiments were conducted in the years 1876 and 1877, the latter proving a bad year for turnip crops. No difference was observed between the effect of animal and mineral phosphates. From the results obtained, the author shows that the effect of insoluble phosphates varied little from that produced by soluble phosphates:—

|  |  |  |  | Yield per acre in kilos. after<br>treatment with |                       |
|--|--|--|--|--|-----------------------|
|  |  |  |  | Insoluble<br>phosphate.                          | Soluble<br>phosphate. |
| 1876. Mean of 30 experiments at 15 places ..           |  |  |  | 17,270   | 18,290                |
| 1877.     "     6                     "     1 place .. |  |  |  | 18,290   | 17,260                |
| 1877.     "     4                     "     "     ..   |  |  |  | 8,430  | 9,860                 |

Addition of nitrogenous manures to the phosphates yielded the following results in 1876 :—

|                           | Sulphate of ammonia<br>with |                        | Chili saltpetre<br>with |                        |
|---------------------------|-----------------------------|------------------------|-------------------------|------------------------|
|                           | Soluble<br>bone-ash.        | Insoluble<br>bone-ash. | Soluble<br>bone-ash.    | Insoluble<br>bone-ash. |
| Mean of 10 experiments .. | 20,720                      | 20,720                 | 21,130                  | 18,699                 |
| „ 2 „ ..                  | 24,880                      | 24,880                 | 23,350                  | 22,350                 |

The increase in the yield produced by the addition of nitrogenous manures is, however, only an apparent one, as it arises merely from an increase of the percentage of water in the product. The same increase in the yield may be obtained when the phosphate is very finely powdered.

The author also finds that the highest percentage of nitrogenous matter and the smallest quantity of sugar was the result of manuring with soluble phosphate, whilst insoluble phosphate produced the exactly opposite effect, and a medium result was obtained when nitrogen had been added to either.

Those plots which were manured in 1876 were left unmanured in 1877 in order to observe the after-effects of the various materials used. It was observed that those fields which gave the best yields in the former year were the least productive in the latter, and *vice versa*. Animal phosphate also appeared to have a better after effect than phosphates of mineral origin. The highest produce as a total of both years was obtained by using raw dried bone-ash, which is more effective when applied in spring than in autumn. The results obtained by the use of this manure show that it is the best that can be applied in the case of turnips.

J. K. C.

**Action of Different Manures on the Yield of Potatoes.** By W. PAULSEN (*Bied. Centr.*, 1879, 106—108).—Sheep's dung produces a yield 50 per cent. higher than that produced by various other artificial manures, and 60 per cent. higher than if no dung be applied. Extra supplies of ammoniacal superphosphate produce no increase, and "compost" does not appear to be capable of producing larger yields than unmanured land. But, on the other hand, manures increase the amount of starch. The number of diseased potatoes was highest in the plots which were unmanured, and more especially high in the crops of "Fürstenwalder;" amongst the "snow flake" potatoes there were also many diseased. Of the seven sorts grown, "Aurora" seems to have been the most satisfactory.

E. W. P.

## Analytical Chemistry.

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**Method for the Continuous Measurement of the Intensity of Daylight, and of its Application to Physiological and Botanical Researches.** By M. KREUSLER (*Biol. Centr.*, 1879, 117—120).—In the first portion of this article an instrument is described whereby the intensity of daylight can be estimated for any hour; it consists of a hollow drum in which is cut a slit parallel to the terrestrial axis; behind this slit is a strip of sensitised paper, across whose surface the slit is caused to pass by means of clockwork. To be able to compare the shades of colour, several tints are produced also on sensitised paper, by causing the direct rays of the sun to fall on the paper at various angles for twenty seconds, this being the length of exposure for each part of the registering paper. An inclination of  $60^\circ$  (cos. 0.5) produces half-tint, &c., the tints being numbered 1, 2, 3—10; 10 representing full sunshine.

In the second portion, the author states that brightness of light is accompanied by increased assimilation on the part of the plant; but this regularity of increase continues only up to the point when the intensity of light is one-eighth that of the full sunshine, and after that assimilation goes on less rapidly, not keeping pace with the increased intensity. Now, as increased intensity of light is accompanied by increased chemical intensity, the former may be used as an indicator of the latter, as regards plant physiology, as it was found that assimilation increased as chemical intensity increased, at first rapidly, but afterwards in a less degree. Sub-aquatic plants are not of value in determining assimilation, as they are not sensitive enough to small changes of light; an apparatus has therefore been devised in which it is possible to expose whole plants to the light, and is on the principle of an aspirator. E. W. P.

**Estimation of Chromium.** By T. WILLM (*Ber.*, 12, 2223—2226).—When chromium is estimated as sesquioxide by precipitation with ammonia, boiling off the excess of alkali, and ignition of the precipitated hydrate, the results obtained are invariably too high if the precipitation is carried on in a glass vessel. The small quantity of lime which is taken up by the ammonia from the glass enables the chromium sesquioxide, during ignition, to combine with the oxygen of the air to form chromic acid. Calcium chromate can be dissolved out of the ignited residue by treatment with hot water. W. C. W.

**Separation of the Heavy Metals of the Ammonium Sulphide Group.** By C. ZIMMERMANN (*Annalen*, 199, 1—16).—*Zinc from the other Metals.*—The solution is made as nearly neutral as possible (this is absolutely essential) with sodium bicarbonate, and mixed with a not too dilute solution of ammonium thiocyanate. After being heated to  $60^\circ$  to  $70^\circ$ , a gentle stream of sulphuretted hydrogen is passed into the liquid at intervals until it smells distinctly of the gas. It is then

left to stand for some hours at a gentle heat, when the whole of the zinc is found to be deposited as sulphide, and perfectly free from the other metals of the group. An excellent method of estimating the zinc is to convert the sulphide into the chloride, and to heat the latter with mercuric oxide, by which means the zinc is converted into oxide and may be weighed as such.

*Iron from Nickel and Cobalt.*—The solution is mixed with excess of ammonium thiocyanate, and sodium bicarbonate is added until the red colour disappears. The iron is thus completely precipitated as ferrous hydrate, and is free from nickel and cobalt. The nickel and cobalt are then separated by Liebig's mercuric oxide method.

*Iron from Uranium.*—The boiling hot solution is mixed with excess of ammonium thiocyanate, and sodium bicarbonate is added until the red colour disappears. The iron is precipitated entirely as hydrate, and is free from uranium.

*Precipitation of Uranium Oxide by Ammonia.*—Addition of ammonia in presence of ammonium chloride causes precipitation of uranium oxide in solution so dilute that the former reagent alone produces no effect.  
G. T. A.

**New Method of Estimating the Air Space in Seeds and Fruits.** By J. ADAMEC and E. KLOSE (*Bied. Centr.*, 1879, 150).—The volume of the sample is calculated from its specific gravity; the volume of the several constituents is calculated from their specific gravity; those added together give the volume of the solid, and, subtracting this from the original volume, the air enclosed is calculated.

E. W. P.

**Composition of Bohemian Beer-wort, determined by Chemico-optical Processes.** By T. HANAMANN (*Bied. Centr.*, 1879, 138).—The author in this paper comes to the conclusion that by the early processes of determination, the amount of dextrin present in wort was too high; by the modern process, the amount is too low; the true quantity is to be found between, and can be closely determined by the polariscope.

E. W. P.

**Determination of the Acid in Sugar of Lead and in Lead Vinegar.** By F. SALOMON (*Dingl. polyt. J.*, 234, 222—226).—What the author claims as novelty in this paper is (1) that as standard acid a solution of acetic acid should be used, which contains exactly 50 grams of acetic anhydride in 1 liter; (2) that the solution of potash used should be equivalent to the acetic acid solution. The following are the details of the method:—10 c.c. of the solution to be examined are treated with an excess of the standard potash in a 100 c.c. flask, and the mixture is made up to 100 c.c. with distilled water. The portion of the lead which is dissolved by the excess of potash used is separated from the hydrate by filtration, and 50 c.c. of the filtrate titrated with standard acetic acid, using phenolphthalein as indicator. In the case of the solution containing sugar of lead, the total acid may be estimated at once, providing the salt is neutral; if acid, it is best to estimate the quantity of free acid with standard alkali, using litmus as indicator in this case. To apply the method to determinations of



acid in lead vinegar, it is necessary to neutralise the basic solution with the titrated acetic acid solution. D. B.

**Analysis of Cinchona Barks.** (*Chem. News*, 40, 209—210.)—  
1. *Ether process.*—1,000 grains of very finely-powdered bark are mixed with sufficient alcohol to form a paste, and when the fibres are thoroughly saturated with the liquid, it is intimately mixed with 500 grains of calcium hydrate, and heated to drive off the alcohol. The dried mass is exhausted successively with ether, the ethereal solution evaporated, and the residue fused at 125° C. The mass is weighed and dissolved in absolute alcohol, and the solution neutralised with standard sulphuric acid (100 c.c. = 10 grams crystalline quinine sulphate). The alcoholic solution of basic quinine sulphate is evaporated to dryness and treated with a quantity of standard acid equal to that previously used; water is added, and the salt completely dissolved by boiling. Animal charcoal to the amount of 15 per cent. of the original weight of bark is then added; the whole digested for 10 minutes, filtered, and washed with acidulated water. The filtrate containing acid quinine sulphate is concentrated, nearly neutralised with dilute ammonia (3 per cent.), and allowed to crystallise. The crystals of basic quinine sulphate are collected and weighed. Weight of air-dried crystals = amount of crystalline quinine sulphate in the bark. Dried at 100°, 85.5 = 100 crystals.

2. *Acid process.*—1,000 grains of finely-powdered bark are treated twice with boiling dilute sulphuric acid, and once with water; the extracts are evaporated to a small bulk, neutralised with milk of lime, and filtered. The residue is dried and boiled repeatedly with alcohol of 90 per cent.; the alcoholic solutions are evaporated to dryness, and the residues treated with acidulated water and filtered; the filtrate is neutralised with caustic soda and shaken with chloroform; the chloroform solution is separated and evaporated in a tared capsule. The residue consisting of the total quantity of quinine, cinchonine, and quinidine is treated with ether to extract the quinine, which is estimated by the ether process. The residue is dissolved in dilute acetic acid, and treated with a concentrated solution of potassium iodide. The precipitate consists of quinidine iodide, of which 100 grains = 71.69 quinidine, or 94.5 quinidine sulphate. The quinidine and cinchonine may be separated by treating the residue with proof spirit, in which the quinidine is soluble, whilst cinchonine and cinchonidine remain undissolved.

Owing to the rapidity with which the ether process may be worked, it can be used with greater advantage than the acid process. The object of the former is to extract that alkaloid only on which the value of the cinchona bark depends, and is achieved without producing amorphous quinine, which is so liable to be formed by protracted boiling, as in the acid process.

Calisaya and red cinchona barks may be analysed by the ether process, but it is not applicable to the Lora or grey barks.

L. T. O'S.

**Estimation of Albuminoid Nitrogen in Fodders.** By F. SESTINI (*Bied. Centr.*, 1879, 711).—The author recommends boiling the

finely powdered substance for one hour in water, to which a few drops of lactic acid have been added, treatment with lead acetate and filtration. The nitrogen is then estimated in the precipitate and the filtrate, the amount contained in the former representing the quantity of albumin present.

J. K. C.

**Enumeration of the Fat Globules in Milk as a Test.** By E. BOUCHUT (*Bied. Centr.*, 1879, 145).—One drop of milk is diluted with 100 drops of water, and this placed in a cell 0.1 mm. deep is examined under the microscope; the globules in a space 0.1 mm. square are counted, the number obtained multiplied by 100,000, and this then gives the number contained in 1 cm. of the original milk. In human milk from 2,200,000 to 5,000,000 globules have been observed, but the average number appears to be from 1,000,000 to 2,000,000. With cow's milk, the results were—

|                    |              |                           |
|--------------------|--------------|---------------------------|
| 1,102,500 globules | 1022 sp. gr. | 24 grams butter per liter |
| 2,205,000       "  | 1032       " | 37       "                |
| 2,400,000       "  | 1030       " | 37       "                |
| 3,700,000       "  | 1030       " | 34       "                |

As human milk varies considerably, it is advisable, in comparing specimens from different individuals, to take five samples on the same day. When 800,000—1,000,000 globules are found in human milk per centimeter, the milk may be considered as good.

E. W. P.

**Foreign Colouring Matters in Red Wine.** By J. NESSLER (*Bied. Centr.*, 1879, 142—145).—The author comes to the conclusion that we are at present not in a position to determine chemically the difference between the colouring matters of madder, bilberry, and grapes. A pure wine reacts differently with the same reagents, the difference depending on the mode of preparation, and the quality of the grape itself.

E. W. P.

**Adulteration of Wine.** By F. LEFEL (*Bied. Centr.*, 1879, 709).—Red beet is often used in conjunction with fuchsine to colour wine. The presence of the former may always be recognised by the author's copper reaction (*Ber.*, 10, 1875).

J. K. C.

**Morphiometric Processes for Opium.** By A. B. PRESCOTT (*Pharm. J. Trans.* [3], 10, 128—130, and 182—185).—The author submits the following assay process for opium; it is essentially the *Huger-Jacobsen's*, but it is modified by a preliminary washing of the opium with benzene, to remove impurities.

The opium is dried at 100° C., until it ceases to lose weight; it is then powdered, and 66.5 grams are placed in a paper filter of 10 cm. diameter in a funnel; benzene is poured in until the powder is covered, and as soon as it begins to drop through, the funnel is stopped, and allowed to macerate for an hour; the benzene is then allowed to percolate, more being supplied, until the whole volume used is 50 c.c. The filter and its contents are dried with gentle heat, until there is no further smell of benzene, and the contents are then transferred to a

weighed flask of 120 c.c. capacity, the filter paper being kept. 20 c.c. of water are added, together with 3 grams of slaked lime, which has been slaked with one-third its weight of water. The contents of the flask are agitated for several minutes, and then uniformly mixed by closing the flask and shaking it. Distilled water is added, until the contents of the flask weigh 74.5 grams, and the flask is heated with occasional agitation for an hour in nearly boiling water; it is then cooled, and the exact weight (74.5 grams) made up again by the addition of water. The solution is then filtered through the paper previously used, into a vessel of about 80 c.c. capacity, marked for a volume of 50 c.c. As soon as exactly 50 c.c. of filtrate are obtained, the contents of the filter being gently squeezed, if necessary, to yield the last few drops, it is mixed with 8 drops of benzene, and 3 c.c. of washed ether, the vessel closed, and the whole agitated; 4.5 grams of powdered ammonium chloride are then added, and as soon as it is dissolved the liquid is once more agitated, and then set aside in a cool place for three and a half hours. The crystalline deposit is filtered through a weighed and moistened filter, and washed several times with a few drops of water; it is then dried at 50° C., washed with 3 c.c. of washed ether, dried again and weighed. The weight of morphine thus obtained may be considered as that contained in 5 grams of opium; this allows for loss during filtration; the percentage is therefore obtained by multiplying the weight found by 20.

The author also submitted different processes for estimating morphine to a comparative trial by analysing several samples by each of the methods; then estimating by Mayer's volumetric method the purity of the morphine obtained, and also determining the morphine remaining uncrystallised in the mother-liquor by extraction with amyl alcohol and titration. Mayer's solution was prepared by dissolving 13.55 grams of dry mercuric chloride and 49.84 grams potassium iodide in water, and making up to a litre; 1 c.c. corresponds to 0.02 of morphine. The morphine precipitates were dissolved in water with acidulated sulphuric acid, and so far diluted that at the end of the titration the solution should be 200 parts to 1 of morphine, this precaution being necessary because of the solubility of the precipitate in water. The author finds that the results obtained by Mayer's process are more accurate than those yielded gravimetrically after purification of the crystals, but they are probably somewhat low. The morphine remaining in the mother-liquor was partially separated by allowing a further time for crystallisation, and the filtered liquid was then well shaken with amyl alcohol in successive portions of 15, 10, and 5 c.c.; the alcohol was separated and evaporated, and the residue titrated by Mayer's solution.

The conclusions arrived at are that hot benzene, if used for the preliminary treatment, occasions a loss of morphine as compared with cold benzene; the cold benzene, however, must be used in limited quantity, since it dissolves some morphine. The omission of the preliminary treatment with benzene leaves the opium-lime mixture loaded with opium wax, and renders the filtration more difficult, and the entire operation less satisfactory, but results after deduction of one-tenth (or one-thirtieth if ether-washed) are fairly in accordance with those

obtained by the modified process of treating with benzene. The *Procter-Staples'* process yielded unsatisfactory results, more especially in the estimation of morphine extracted from the mother-liquor by amyl alcohol. The author suspected that something besides the alkaloid, which acted on Mayer's solution, was taken up by amyl alcohol. It was found more satisfactory to extract the mother-liquor obtained by *Staples'* process, first with benzene, and afterwards with amyl alcohol. By *Hager's* process the filtrate contains in solution 1.9 times as much as pure water, and by *Staples'* process 2.45 times as much. *Schachtrupp's* process for estimating morphine and narcotine in opium (*Zeits. Anal. Chem.*, 1868, 7, 509), was also submitted to examination; the author pronounces it to be untrustworthy and inexpedient; the experiments made by this process, however, proved that benzene does not extract the whole of the narcotine from opium, unless an alkali is present, and therefore the preliminary treatment with benzene does not dispense with purification of the morphine crystals by washing with ether freed from alcohol and acetic acid by recent agitation with water; the impurities left in the morphine may then be considered as counterbalancing the morphine left in the mother-liquor, and removed by washing. F. C.

**Valuation of Tincture of Opium.** By A. B. PRESCOTT (*Pharm. J. Trans.* [3], 10, 66).—The author determined the opium in twelve different samples of the tincture, employing two different processes for each sample, viz., *Hager's* and *Staples'*.

The modified *Hager's* process was carried out as follows:—The specific gravity of the tincture was taken; then 25 grams were evaporated nearly to dryness on the water-bath, triturated with 1 gram of freshly slaked lime, and after adding 24 c.c. of water, the mixture was heated on the water-bath for an hour. The whole was then transferred to a wetted filter, and the residue washed on the filter with warm water, until the washings were nearly colourless; the filtrate, after being concentrated on the water-bath to 25 grams, was transferred with rinsings to a wide-mouthed bottle, and mixed while warm with 1 c.c. of ether and 3 drops of benzene; 1.1 gram of ammonium chloride was then dissolved in the liquid, and it was set aside for 24 hours. The liquid was now well shaken, to detach crystals from the sides of the bottle, and the crystals collected on a weighed filter, washed with about 8 c.c. of distilled water, dried at 50° C., and weighed. If *Hager's* plan is followed of allowing only three hours for the crystallisation of the morphine, the author prefers to wash the crystals with ether, and weigh them, the impurities present counterbalancing the morphine left in solution.

According to *Staples'* method, after estimating the specific gravity, 25 grams were evaporated to half the bulk on the water-bath, and 24 hours allowed for the subsidence of the tarry matters; the liquid was decanted through a filter into a wide-mouthed bottle, and the tarry residue washed with 4 c.c. of water, the washings being added to the filtrate. An equal volume of alcohol of sp. gr. 0.835, and 1.3 c.c. of ammonia solution of sp. gr. 0.96, mixed with 1.7 c.c. of alcohol, were then added, the bottle stoppered and well shaken, and set aside.

After about four days the morphine crystals were filtered off, rinsed with 4 c.c. of diluted alcohol, dried at 50°, and weighed. The crystals were afterwards washed with 8 c.c. of ether, and weighed again; the ether removed about one-tenth by weight of the crystals.

The author concludes that *Stuples'* process yields the best crystals of morphine, but considers that it is little if at all preferable to *Hager's* method. F. C.

**Analytical Examination of Tinctures.** By A. H. ALLEN (*Pharm. J. Trans.* [3], 9, 1035—1037).—Tinctures are made with spirits of two alcoholic strengths. For some, rectified spirits, containing 84 per cent. by weight of absolute alcohol, equivalent to 155.5 per cent. of proof spirit, is used; for others proof spirit, containing 49 per cent. by weight of absolute alcohol, is sufficiently strong. Alcohol being frequently the most expensive item in the preparation of tinctures, it is liable to be economised, and this will often lead to an insufficient quantity of the drug being dissolved. Hence the determination of the proportion of alcohol present in a tincture is often of importance. With many tinctures, the alcohol can be readily separated by distillation and estimated by taking the specific gravity of the distillate, volatile alkaline or acid substances being retained during distillation by previously making the tincture acid or alkaline respectively. Tinctures containing volatile essential oils cannot be examined by distillation, but the oil can usually be precipitated by a sufficient dilution with water, and if it remains suspended in the liquid it may then be separated by adding a few drops of strong calcium chloride solution and some sodium phosphate and stirring vigorously; the precipitated calcium phosphate carries down the oil globules and clarifies the liquid, which is then run through a dry filter and distilled. In some cases sodium carbonate is substituted for sodium phosphate when an acid is to be retained during the subsequent distillation. The percentage of alcohol present is best stated in terms of proof spirit.

The process was tested on tincture of myrrh, which had been prepared for the purpose. The alcohol found was about 6 per cent. too low, but this discrepancy was explained by the fact that myrrh causes a considerable expansion of the volume during solution in spirit, and after estimating and allowing for this expansion exact results were secured. A similar result was obtained with camphor. Experiment showed that camphor dissolved in alcohol without sensible change of volume, the volume of the tincture being equal to the sum of the volumes of the spirit and the camphor. Hence it appears that the spirit causes the camphor to liquefy and mingle as a liquid with the spirit. In consequence of this peculiarity, the proportion by volume of proof spirit contained in spirit of camphor will be 0.9 of that present in the alcohol used in its preparation, and there is no doubt that a similar correction ought to be applied in certain other cases. The distillation method, when applied to spirit of camphor, is also rendered inexact by some of the camphor remaining unprecipitated, owing to its solubility in water.

The author found a deficiency of alcohol in a sample of "compound tincture of camphor," and this led to a deficiency also of oil of anise,

since the spirit was too weak to dissolve the full proportion of oil. This tincture was examined by diluting with water, clarifying with calcium chloride and sodium carbonate solutions, distilling the alcohol, and estimating benzoic acid in the residue by acidifying it and shaking several times with ether. On evaporating the ether, the benzoic acid was left in a pure state; the opium was roughly estimated colorimetrically by adding proof spirit and a few drops of ferric chloride, and comparing with a similarly treated standard opium solution. The percentage of alcohol found in this tincture by the distillation process never exceeded by two degrees that deduced from the density of the original tincture. The proportion of oil of anise present may be roughly judged by the readiness with which the liquid is precipitated on dilution with water. With a proper proportion of oil, precipitation occurs on very slight dilution.

F. C.

## Technical Chemistry.

**Recent Improvements in the Iodine Industry.** By B. WETZIG (*Dingl. polyt. J.*, 234, 216—220).—The heavy pressure which has been put on the European market by the production of iodine in South America is mostly due to the fact that the treatment of the plant, its burning to ashes, and the lixiviating operations are conducted in a very imperfect manner in Europe. Various methods have been proposed whereby the loss of iodine, experienced in the first treatment to which the plant is subjected, is reduced considerably. The plants are generally collected during the winter months, and are dried and burnt to ashes in June and July. During this interval a large quantity of iodine is lost through the action of fogs and rain on the plant. Pellieux and Maze-Launecy subject the plant to a fermentation process, whereby the loss of iodine is reduced considerably in the after treatment. At the beginning of the fermentation, all sulphides present are said to be converted into alkaline sulphides or hydrogen sulphide; the latter acts on the organic iodine-compounds which may be present, forming hydrogen iodide. This body destroys all alkaline sulphides, potassium and sodium iodides being the final product. Similar methods have been proposed by Thiercelin and Herland.

As to the separation of iodine from varec, potassium chloride has been adopted very largely, the results being most satisfactory. In practice the proportion of potassium chloride to the iodine is 1 : 4 (theory 1 : 6).

It is stated that the methods which are generally used for determining iodine are of but little practical value in varec analyses. Wallace and Lamont's method of precipitating iodine with silver nitrate and washing with ammonia gave satisfactory results; however, Fresenius's method is the simplest, safest, and best. Instead of dissolving nitrous acid in sulphuric acid, the author uses a solution of

ferric chloride with the addition of a small quantity of sulphuric acid for precipitating the iodine.

D. B.

**Introduction of Nitric Acid into the Sulphuric Acid Chambers along with the Steam.** By M. LIEBIG (*Dingl. polyt. J.*, 233, 61—63).—The author says his apparatus has stood the test of experience in one sulphuric acid manufactory in Westphalia. It consists of a leaden steam-pipe with platinum nozzle whose opening is from 4 to 5 mm. diameter, which penetrates the leaden wall of the chamber for 5 or 10 cm. in a straight line. Immediately underneath this, and also penetrating the chamber wall, is a glass tube 5 mm. diameter drawn to a fine point; this tube is bent upwards, so that the point terminates in the centre of the opening in the steam-pipe; outside the leaden chamber, the glass tube is bent downwards at an angle of  $30^\circ$  from the horizontal, and is passed at the same angle into another tube, the junction of the two tubes being made tight by a piece of india-rubber tube; the tube into which it passes is bent into a U and connected with the bottom of the apparatus for regulating the flow of acid. This consists of a glass bulb, into the top of which projects a tube of 2 mm. diameter, and furnished with a glass stopcock having a projecting arm moving over a graduated scale so as to regulate the flow of acid. The tap is connected with a syphon passing to the bottom of a flask filled with nitric acid. When the glass tap is opened sufficiently to allow the required amount of nitric acid to be delivered from the flask into the bulb, and the steam is turned on, it blows across the fine opening in the glass tube, producing a partial vacuum in the bulb; the nitric acid in the flask then rises in the syphon tube, passes through the stopcock and bulb, and issues at the point of the glass tube fixed in front of the nozzle of the steam-pipe, when it is blown by the steam into a spray which mixes thoroughly with the sulphurous acid coming from the burners; by this means the exact quantity of nitric acid projected into the chamber can be accurately determined and any excess obviated.

W. T.

**Observations on Sulphur-baths.** By P. DE CLERMONT and J. FROMMEL (*Bull. Soc. Chim.* [2], 31, 485.—Becquerel has stated that the electromotive force of polysulphides to monosulphides is in the proportion of 163 to 248. As the therapeutic action of sulphur-baths has been ascribed to their electromotive force, some physicians have prescribed baths of sodium monosulphide instead of polysulphide.

The authors have shown that the amount of sulphuretted hydrogen evolved from the bath of monosulphide bears to that evolved by polysulphide, the inverse proportion to their electromotive forces. By adding manganese chloride to a solution of monosulphide of sodium at  $34^\circ\text{C}$ ., 0.0118 gram of sulphuretted hydrogen was liberated, whilst from a solution of polysulphide of similar strength, 0.0206 gram escaped. As the polysulphide is less efficacious from the medical point of view than the monosulphide, it is evident that the quantity of sulphuretted hydrogen liberated is not, at least in the case cited, proportional to its therapeutic action, and to the strength of the electric current.

W. R.

**Use of Copper Phosphide in the Refining of Copper.** By C. RÖSSLER (*Dingl. polyt. J.*, 233, 48—53).—The object of this process is to separate all the oxide of copper from the metal, and so to make it tougher and more ductile. Amorphous and ordinary phosphorus have been proposed for this purpose, but their use is now superseded by that of copper phosphide of known composition: this has been employed several years at Chatham dockyard with satisfactory results. The advantages of using copper phosphide in preference to free phosphorus are, that with the former the whole of the phosphorus present is available for reducing the copper oxide present in the molten metal, and the possibility of accurately determining beforehand the quantity of copper phosphide required; the danger to the health of the workmen caused by the use of phosphorus is also avoided.

According to Hampe, when copper phosphide comes in contact with cupric oxide, one equivalent of phosphorus combines with the oxygen of five equivalents of copper oxide, forming phosphoric anhydride, which combines with another equivalent of copper oxide, forming copper phosphate, which rises to the top of the molten metal as a fluid slag.

In the refining furnace 1,700 kilos. of copper was first "poled" in the usual way until the required point of deoxidation had been reached, which was ascertained by taking a quantity out and testing it. The quantity of phosphide added was 9 kilos., containing 11·7 per cent. of phosphorus. It was introduced in five separate portions, the whole then stirred by a protected iron crook, covered up with wood charcoal, and the door and every other opening of the furnace closed. A portion was then drawn off, and when cold tested by being bent by repeated strokes of the hammer. This showed a marked difference in the constitution of the metal *before* and *after* the addition of the phosphide. In the latter case it had an amount of toughness which was quite astonishing. Its cleavage was finely toothed, of salmon-red colour, and silky lustre, like that of chemically pure copper, in contrast to the cleavage of the other specimen, which could not be distinguished from that of copper refined in the ordinary manner for commercial purposes.

The specific gravity of the sample *before* the addition of copper phosphide was 8·731, and *after* the addition it was 8·906. With a view to determine the actual percentage of oxygen in each sample, portions of each were ignited in a stream of hydrogen. The loss of weight in the sample taken *before* the addition of the phosphide was 0·190, and the loss *after* was 0·042 per cent. The author infers that the whole, or at least part, of the loss in the latter was due to the phosphorus and not to oxygen.

The author further ascertained that much less than the theoretical quantity of copper phosphide required to decompose the oxide present suffices to produce the necessary deoxidation, and this is owing to the fact that when the copper phosphate comes to the surface, as it does in small, very fluid drops, it meets with and is reduced again to phosphide by the action of the red-hot charcoal which is put on the surface, and is again absorbed by the metal, and so repeats its deoxidising action. The minimum quantity of phosphide required to do



the work can therefore only be determined by practical experience. Its use, however, does not end here, because, when the metal is cast into the mould, it protects the casting from the action of the oxygen of the air, and only ceases to act when it has come entirely to the surface in the form of phosphate of the protoxide of copper.

W. T.

**On Belgian Phosphorites.** By A. PETERMANN (*Bied. Cent.*, 1879, 53—57).—Of the four sorts of phosphorites which occur at Ciply, in Belgium, "craie grise," containing 11.25 per cent.  $P_2O_5$ , occurs in largest quantities. It appears to be almost insoluble in solutions of various salts, and when used in the raw state as a manure is of no great value.

E. W. P.

**On Cement.** (*Dingl. polyt. J.*, 234, 473—478).—Tomei has studied the question as to the influence which sulphates are said to exercise on the time of setting and the firmness of cement, and concludes that the addition of sulphates is not favourable, as it retards the setting and decreases the firmness of cement.

Erdmenger in discussing the points as to the methods of improving the quality of cement, especially by stowing it or adding various substances to it, gives a series of experiments which show that cement can often be improved very materially by the addition of gypsum, &c.

Behrmann has tried the influence of sea water on cement and finds its action favourable, especially on Roman cement.

D. B.

**Peculiar Changes of Gas-pipes.** By K. BIRNBAUM (*Dingl. polyt. J.*, 234, 460—463).—At the St. John Gas Works, near Saarbrück, some gas-pipes which had been in use for ten years showed peculiar phenomena. The cast-iron of which the pipes were made had assumed the form of a regular, brittle, and graphite-like mass of magnetic oxide, which could be cut with a knife and had a shining surface. The latter disappeared after a few weeks' exposure to the air.

The author explains this alteration by the fact that, owing to the softness of the soil, it was necessary to surround the pipes with some hard material in order to keep them in their position, and for this purpose cinders were employed. These were obtained from the Saar coals, which are noted for the large amount of pyrites they contain. The latter coming into contact with rain-water, and also being partly exposed to atmospheric influences, readily acted on the metal and brought about these changes.

D. B.

**Action of Water on Lead Piping.** By E. REICHARDT (*Arch. Pharm.* [3], 15, 54—63).—The examination of a lead pipe which had been employed during 300 years at Andernach for the conveyance of water, showed the formation of a coating on the interior surface 0.5 mm. thick; the colour of this coating was yellowish-white, and had the composition:—

| PbO.   | BiO <sub>3</sub> . | OsO.  | CuO.  | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> . |
|--------|--------------------|-------|-------|--------------------------------|----------------------------------|
| 73.962 | 0.453              | 0.120 | 0.323 | 1.552                          | 1.035                            |

| CaO.  | MgO.  | P <sub>2</sub> O <sub>5</sub> . | CO <sub>2</sub> . | Cl.   | H <sub>2</sub> O. |
|-------|-------|---------------------------------|-------------------|-------|-------------------|
| 1.095 | 0.283 | 8.446                           | 1.110             | 1.254 | 6.141:            |

besides organic matter = 0.388; insoluble SiO<sub>2</sub> and clay = 4.399. The source of the phosphoric acid is unknown, as the analysis of the water at the present time, which has a hardness = 5.25, shows no trace of it. This encrustation has a peculiar fatty acid smell, but no definite organic compound could be obtained from it; the presence of this substance, whatever it may be, is considered to be due to eels, which were formerly employed to free the pipe from rootlets with which it became clogged.

Concerning the various modes of coating the interior of lead pipings, so as to preserve them from the action of water, the author has made experiments with piping coated with a layer of lead sulphide in the interior surface, by the action of an alkaline sulphide. He finds that distilled water becomes contaminated in such a pipe, but this does not occur if the water contains large quantities of magnesium and calcium carbonates. On the contrary, this water deposits salts on the interior, and preserves it; but they are removed together along with lead by water containing carbonic acid. E. W. P.

**Tungsten-Manganese Bronze.** By F. P. VENABLES (*Chem. News*, 40, 187—188).—An analysis of an alloy from Hanover, bearing the above name, proves that it contains no manganese, and only an insignificant quantity of tungsten. It consists of ordinary gun-metal, in which part of the tin is replaced by zinc, as is seen from the results:—

| Cu.   | Sn.  | Zn.  | Fe.  | W.   |
|-------|------|------|------|------|
| 86.51 | 9.04 | 3.47 | 0.26 | 0.23 |

It is of a light golden-yellow colour, and close grain, and is susceptible of a fine polish. Its sp. gr. = 8.64. L. T. O'S.

**Petroleum.** By H. HÖRLER (*Dingl. polyt. J.*, 234, 52—61).—This paper is based on a report to the authorities of Zürich by V. Meyer respecting the sale of petroleum and other inflammable liquids. Various points are taken into consideration, such as the limit of temperature at which petroleum ignites, the construction of petroleum lamps and stoves, the size of petroleum stoves, their distance from dwelling-houses, and regulations requisite in case of fire.

As to the flashing point of petroleum, it is stated that although a large number of apparatus for determining this point are known, the results obtained are very unsatisfactory. Meyer recommends the use of an apparatus, which is said to give the true flashing point of inflammable liquids. A corked glass cylinder is fitted with two thermometers, one dipping in the petroleum, the other being above it. One-tenth of the cylinder only is filled with the petroleum to be examined. It is next placed in warm water for a few minutes, then taken out and well shaken, until the temperature of both thermometers is the same. The cork is now removed and a flame introduced into the cylinder. The flame burns at the end of a small glass tube drawn out to a very fine

point. If the vapour ignites the operation is repeated at a lower temperature, until a point is reached at which the vapour no longer ignites.

Meyer is of opinion that the flashing point of petroleum should not exceed 36°. D. B.

**Improvement of Italian Tobacco by permeating the Leaves with the Juice of Exotic Tobacco.** By A. DE NEGRI (*Gazzetta*, 9, 418—420).—The author proposes to place the indigenous leaves in an autoclave, and after exhausting the air to allow a strong infusion of exotic leaves to flow into the apparatus, subsequently increasing the pressure to two or three atmospheres, so that the juice may thoroughly permeate the leaves. When the operation is finished, the leaves are removed from the liquid and dried in a centrifugal machine. In this way the aroma is greatly increased, whilst the exotic leaves from which the infusion was made, if only partly exhausted, are still useful, although of somewhat less value. C. E. G.

**Preparation of Wine.** By A. BLANKENHORN and Others (*Bied. Centr.*, 1879, 706—707).—The authors recommend the aëration of must which is rich in sugar and albumin during the earlier part of the fermentation. The colouring matter of red wine is much more soluble between 15 and 20°C. than between 0 and 10°C. J. K. C.

**Bleaching of Jute.** By M. SINGER (*Dingl. polyt. J.*, 234, 486).—The author recommends the following method:—The yarn is first placed into a weak slightly warm soap-bath for 10 minutes, and transferred to a chloride of lime bath of 1·0035 sp. gr. After 40 minutes, the jute is taken out and the operation repeated, if necessary. Finally, it is washed with warm, then with cold water, and dried in the air. D. B.

**Application of Potatoes and Undried Malt in the Preparation of Yeast.** By J. KRIEGER-DELFT (*Bied. Centr.*, 1879, 718).—The mash used for preparing yeast should not contain much more than 10 per cent. of fermentable sugar, with peptone and ash in proper proportions. The author recommends also the use of undried in preference to dried malt. J. K. C.

**Influence of Light on Beer.** By O. NEY (*Bied. Centr.*, 1879, 152).—Black, yellow, blue, white, green represent the order in which the colours influence beer, when it is enclosed in bottles of the above colours. Green has least influence, and therefore it is recommended that green bottles are the best in which to store beer. E. W. P.

**Adulteration of Rye Bran with Rice Husks.** By J. KÖNIG (*Bied. Centr.*, 1879, 149).—A specimen of rye bran was found to contain 40 per cent. of rice husks, causing the albuminoids to fall from 14·7 to 9·6, and raising the fibre from 5·7 to 17·5. E. W. P.

## General and Physical Chemistry.

**Dark Lines in the Solar Spectrum on the Less Refrangible Side of G.** By J. C. DRAPER (*Am. J. Sci.* [3], 17, 448—452).—The author refers to a former paper on this subject (*Am. J. Sci.*, 16, 256—265, this Journal, 1879, Abst., p. 997). He now discusses the region of the solar spectrum between  $\lambda$  4316 and  $\lambda$  4320 of Ångström's scale. Five photographs, taken in November, 1878, and January and February 1879, show faint lines in this region which agree in position with lines in the electric spectrum of oxygen. Similar lines are visible in Rutherford's photograph of the same region, and in Christie's map of the prismatic spectrum. A diagram is given showing the coincidence of the lines noticed by these three observers, with the lines in the oxygen spectrum as observed by Ångström, Draper, Plücker, and Huggins. A table is also given of the solar lines between  $\lambda$  4313 and  $\lambda$  4325, in which all the lines corresponding with those of known elements are marked. The author considers (1) that the regions in the solar spectrum at  $\lambda$  4317 and  $\lambda$  4319, claimed as bright lines of oxygen, are not as bright as others in their immediate vicinity; (2) that the solar spectrum shows faint dark lines in the region about  $\lambda$  4317 and  $\lambda$  4319; (3) oxygen is the substance which can produce dark lines in this region, therefore we must attribute them to the presence and action of that element.

J. M. H. M.

**Ultra-violet Limit of the Spectrum at Various Heights.** By A. CORNU (*Compt. rend.*, 89, 808—814).—From photographs of the solar spectrum taken at different heights, the author draws the following conclusions:—The ultra-violet limit of the solar spectrum varies to a small extent with the height above the sea-level, owing to the absorptive power of the atmosphere for ultra-violet rays. The rate of variation corresponds to theoretical values deduced from the hypothesis of a homogeneous absorbing atmosphere, provided equally clear days be chosen. The extension of the spectrum expressed in wave-lengths is one-millionth of a millimeter for a rise of about 900 meters, within the limited differences of height observed by the author.

W. R.

**Examination of Essential Oils.** By W. N. HARTLEY and A. K. HUNTINGTON (*Chem. News*, 40, 269).—The following is a list of substances examined by the authors with respect to their optical properties:—

*Oils and Hydrocarbons transmitting Continuous Spectra.*—Australene from oil of turpentine; birch-bark, cajuputene dihydrate, caraway hydrocarbon (No. 2), calamus, citron, citronella, cedar-wood, cedrat hydrocarbon, cubebs, elder, hesperidene from oil of orange peel, Indian geranium, juniper, lavender, lign-aloes, *melaleuca ericifolia*, menthol from oil of mint, nutmeg hydrocarbon, oils of patchouli (Nos. 1 and 2); rose, rosewood, rosemary, santal wood, terebene, terebenthene, vitivert. In these experiments, photographs were taken of the spectrum transmitted by the undiluted liquid, and then of that transmitted by

the liquid in various states of dilution, the dilutions ranging in some cases from 1 in 50 to 1 in 500,000 volumes of alcohol.

*Hydrocarbons showing the Absorption-bands of Cymene.*—Thyme, lemon, nutmeg, caraway (No. 1).

*Substances showing Strong Bands of Absorption in the Spectrum transmitted by Dilute Solutions.*—Oils of aniseed, bay, bergamot, bitter almonds, cassia, cloves, peppermint, pimento and thyme. Carvol, the oxidised derivative of caraway oil, myristicol, the same from nutmeg oil, and blue oil of patchouli.

The authors attach great interest to the examination of these bodies, since they consider it to be proved from the character of the spectra they transmit, that the nucleus of menthol is a terpene, whilst the benzene ring is the inner basis of carvol and myristicol. Bergamot appears to be a terpene mixed with some derivative of the aromatic series; but the oil of peppermint, on the other hand, is essentially a substance belonging to this latter class.

The following is a summary of the author's observations with regard to the terpenes:—

(1.) The terpenes with the composition  $C_{10}H_{16}$  possess in a high degree the power of absorbing the ultra-violet rays of the spectrum, although they are inferior in this respect to benzene and its derivatives, to which class of bodies they are closely allied.

(2.) Terpenes with the composition  $C_{15}H_{24}$  have a greatly increased absorptive power for the more refrangible rays, that is to say, they withstand dilution to a greater extent, the greater the number of carbon atoms in the molecule.

(3.) Neither the terpenes themselves nor the oxidised nor hydrated derivatives occasion absorption-bands under any circumstances when pure, but always transmit continuous spectra.

(4.) Isomeric terpenes transmit spectra which usually differ from one another in length, or show variations on dilution.

(5.) The process of diluting with alcohol enables the presence of bodies of the aromatic series to be detected in essential oils, and in some cases even the amount of these substances present may be estimated.

D. B.

**Ultra-violet Absorption Spectra of Ethereal Salts of Nitric and Nitrous Acids.** By J. L. SORET and A. A. RILLIET (*Compt. rend.*, 89, 747—748).—The nitrates of ethyl, isobutyl, and amyl, have a very great absorptive power for the ultra-violet rays, as is seen from the table:—

| Rays of<br>cadmium. | Wave-lengths. | Thickness of liquid required to produce<br>extinction with nitrate of |                  |              |
|---------------------|---------------|---|------------------|--------------|
|                     |               | Ethyl.<br>mm.   | Isobutyl.<br>mm. | Amyl.<br>mm. |
| 12                  | 325·8         | 15·6  | 14·45            | 9·9          |
| 13                  | „             | 2·0   | 1·9              | 2·3          |
| 14                  | „             | 0·7   | 0·85             | 0·92         |
| 17                  | 274·7         | 0·22  | 0·37             | 0·25         |
| 18                  | 257·2         | 0·07  | 0·2              | 0·07         |

The alcoholic solutions of the nitrates (5 grams per litre) are more

transparent than the undiluted liquids, and are more fit for comparison with the metallic nitrates, yet there exists some difference in chemical construction of the two classes of chemical compounds, the maximum of absorption between the lines 12 and 18, so distinctly recognisable for calcium nitrate both in alcoholic and aqueous solutions, is absent with the ethers, which are more transparent for the rays 12—14, less transparent for the rays 17—20, and again more transparent for the rays 22—24.

Thickness of liquid required to produce extinction  
with alcoholic solution of nitrate of

| Rays of<br>cadmium. | Wave-<br>lengths. | Calcium.<br>mm. | Ethyl.<br>mm.                                 | Isobutyl.<br>mm. | Amyl.<br>mm. |
|---------------------|-------------------|-----------------|---|------------------|--------------|
| 12                  | 325.8             | 60.3            | { ray passes through a thickness of<br>0.1 m. |                  |              |
| 13                  | "                 | 15.1            | 57.95   | 59.7             | 37.6         |
| 14                  | "                 | 7.9             | 17.1  | 17.85            | 15.0         |
| 17                  | 274.7             | 20.35           | 7.1   | 7.82             | 5.72         |
| 18                  | 257.2             | 40.05           | 4.9   | 3.97             | 3.7          |
| 20                  | "                 | 7.82            | 3.52  | 2.6              | 1.9          |
| 22                  | 232.2             | 0.52            | 0.57  | 0.45             | 0.32         |
| 24                  | 226.6             | 0.05            | 0.15  | 0.15             | 0.15         |

The vapours of the ethereal nitrates show absorbing powers even at the ordinary temperature.

Solutions of nitrites of amyl and ethyl act very energetically on the ultra-violet rays: the alcoholic solution of amyl nitrate gives rise to an absorption spectrum, there being six bands at nearly equal distances between the solar rays H and R, varying in distinctness. The first and sixth between H—L and Q—R are the most indistinct. The second and fifth at M and P—Q are more distinct, and the third and fourth at N and O are most distinct. Ethyl nitrite gives a similar spectrum.

The vapours of amyl nitrite at the ordinary temperature present the same spectrum as the alcoholic solution, but sharper.

L. T. O'S.

**Electric Discharge of the Chloride of Silver Battery.** By W. DE LA RUE and H. MÜLLER (*Compt. rend.*, 89, 637—641).—By a series of experiments on the discharge in air, hydrogen, and carbonic anhydride, details of which are given, the authors have established that there is a minimum pressure for each gas corresponding with a minimum resistance to the passage of the discharge, but if the pressure be diminished beyond this minimum, the resistance increases with extreme rapidity. Although there appears to be no condensation or expansion of the gaseous medium in the neighbourhood of the electrodes, the discharge is accompanied by a sudden expansion of the gas, which, however, does not seem to be due merely to heating, as it lasts the whole time of the discharge, and ceases instantaneously with it. The relation which exists between the pressure and the difference of potential necessary to produce discharge between two plane surfaces at a constant distance, may be represented by a hyperbolic curve, taking

the pressures as abscissæ and the numbers of elements as ordinates. It is the same for the difference of potential and the distance of disruptive discharge when the pressure is constant. The resistance to the discharge between two plates varies as the number of interposed molecules. The law is the same for points. The authors have previously shown, that for a constant pressure equal to that of the atmosphere, the potential varies as the square root of the distance. With a constant pile of 11,000 elements, the distance at which disruptive discharge takes place, varies inversely as the pressure, from 1—15 mm. The electric arc and the stratified discharge in a vacuum appear to be modifications of the same phenomenon. C. E. G.

**Phosphorescence produced by Electrical Discharges.** By E. WIEDEMANN (*Ann. Phys. Chem.* [2], 9, 157—160).—Most of the platinocyanides exhibit fluorescence under the influence of electrical discharges, but the fluorescence is dichroic only as the result of a partial decomposition. Dichroism is induced in barium platinocyanide without any electrical action, by placing the salt in a vacuum for a time. The author attributes this effect to the loss of water, by which loss the optical differences of the several directions in the crystals are more strongly brought out. That dichroism is so much more quickly developed in the salt when it is subjected to electrical discharges, he explains by the warming of the crystals by the discharge. The superficial parts of the crystals thus losing their water become dichroic, whilst the deeper-lying parts fluoresce under the influence of the electric discharge.

These experiments were suggested by a research of Crookes's, from whose view of the cause of the phenomena, however, the author dissents. Instead of a stream of projected molecules, we have here, the author contends, to do with electrical disturbances or waves, communicating their motion to the ether of the solids in which vibrations are thus set up, that appear partly as heat, partly as light. A striking proof of the incorrectness of Crookes's theory is an experiment in which the positive current of a Holtz machine is passed through a discharge-tube, made with *thick* glass, in such a manner that it may be diverted within the tube by the finger. A feeble phosphorescence then appears in the inside of the tube, but on the outside a very bright green light is seen. Closely connected with this phenomenon, is that which appears when a spherical positive electrode is used within a glass globe, and a collecting point touches the external surface of the globe. On the opposite part of the globe is seen a well-defined shadow of the electrode, surrounded by a circle of beautiful green rays. The starting point for a theory of these phenomena is supplied in Maxwell's equations (*Wied. Galv.*, p. 1226). An electrical discharge effected by the motion of material particles is out of the question, as the velocity of electricity in gases is immensely greater than that of any molecular motion whatever. The reflection of the negative discharge from surfaces on which it impinges, is likewise in accordance with Maxwell's theory, if we attribute to the waves of electric polarisation sufficient energy; and that they do in fact possess this may be inferred from their melting the glass upon which they strike. R. R.

**Action of Ozone on some Noble Metals.** By A. VOLTA (*Gazzetta*, 9, 521—532).—In 1844 Schönbein, whilst studying the action of ozone on some of the noble metals (gold, silver, and platinum) found that they became polarised negatively, and in a greater degree as the metal was less oxidisable; this polarisation, moreover, was not due to any peculiar electrical state of the metal, but to the presence of ozone.

The author's method is to take two plates of the metal having the same area, and after exposing one of them to the action of ozone for a certain time, to connect the two with interposed galvanometer, and to plunge the two plates into a vessel containing distilled water.

When *silver* is submitted to the action of moist ozone, the surface becomes coated with black silver peroxide, as Andrews and Tait have observed; but when the ozone is dry, no sensible decomposition of the ozone can ever be detected, although the chemists above mentioned state that the silver is not oxidised, but that the ozone is completely decomposed by the metal. The polarising action of the ozonised silver is found to be invariably negative, whether dry or moist ozone had been used, and there is a deviation of the galvanometer, persisting for some time after the immersion of the plates.

*Gold* is quite unaltered by ozone, whether moist or dry, and the gas is also unaffected by the metal. The polarisation is always negative, but there is no permanent deflection of the galvanometer, as with ozonised silver.

With *platinum* both the ozone and the metal are unaltered. The polarisation is negative, and there is a permanent deflection, but this is much more feeble than with silver.

With *palladium* which is quite free from hydrogen, neither the gas nor the metal is attacked, if the former is dry, but in moist ozone the surface of the palladium becomes covered with an iridescent film, resembling that formed on steel when it is heated; like the other noble metals, palladium is negatively polarised, and it gives a large permanent deflection.

Hydrogenised palladium, even after the action of ozone, is found to be polarised positively, and to give a large permanent deflection, which is very persistent, lasting for days. Hydrogenised platinum behaves in a similar manner, but the deviation is not so persistent.

Dry ozone attacks *mercury* readily. When a tube containing the metal is plunged into the ozonised oxygen, the meniscus instantly disappears, and the surface becomes quite plane; after a few minutes' contact with the ozone, however, the edges become depressed, and the meniscus again reappears with a clean surface, the convexity gradually increasing until it far exceeds the normal curvature; this lasts for a couple of hours, and then the meniscus returns to its ordinary state. This phenomenon the author believes to be electrical, the period of maximum convexity corresponding with the maximum polarity of the metal; this, as in the case of the other metals, is negative, but there is no permanent deflection. Analogous results were obtained with moist ozone, but they were much less strongly marked. C. E. G.

**An Electro-Capillary Thermometer.** By E. DEBBUN (*Compt. rend.*, 89, 755).—The principle on which this instrument is based



is that of Lippmann's electrometer, in which any mechanical movement which alters the form of the mercury meniscus cause an electric current.

A fine capillary thermometer tube is filled with acidulated water, and mercury introduced so as to form a chain of beads, the first and last of which are in connection with platinum wires. When the water expands or contracts it pushes the globules, and in consequence of their contact with the sides of the tube, distorts them, when a current is generated in the direction of the expansion or contraction of the water. This current may be measured on a Lippmann's electrometer, and thus the variation of temperature registered. The advantages of this instrument are (1) the thermometer can be placed in one spot, and observation taken in another; (2) it works without a battery, and is very sensitive.

L. T. O'S.

**Mendeleeff's Periodic Law and the Magnetic Properties of the Elements.** By T. CARNELLEY (*Ber.*, 12, 1958—1961).—*Those elements which belong to the even series of Mendeleeff's classification of the elements (Ann. Chem. Pharm. Suppl.*, 8, 133; *Watts's Dictionary of Chemistry, Sec. Supp.*) are always paramagnetic, whereas those which belong to odd series are always diamagnetic. This rule holds good with all the 38 elements to which it can at present be applied. In the case of the odd members of the same group, the diamagnetism increases with the atomic weight.

T. C.

**Thermal Absorption and Emission of Flames, and the Temperature of the Electric Arc.** By F. ROSETTI (*Compt. rend.*, 89, 781—783).—Flame is very diathermous, and consequently its absorbing power for heat-rays is small. If the radiation from a flame (luminous or non-luminous) traverses another of the same nature, having a thickness of 0.01 m., the coefficients of absorption and transference are respectively 0.135 and 0.865.

The transference and absorptive power decrease and increase respectively, in proportion to the thickness of the flame. An infinitely thick flame is athermous, and its absorptive power unity. This limit is nearly reached with flames of finite thickness, for a flame 1 m. in thickness is almost completely athermous to rays from a flame of the same nature.

The formula  $y = a \frac{1 - k^e}{-\log k}$ , represents the intensity of radiation of a flame having a given thickness  $e$ , expressed in centimeters. The coefficient of transference  $k = 0.865$ ;  $a =$  a constant, the value of which depends on the nature of the flame.

The intensity of radiation of a luminous white flame of infinite thickness, compared with the intensity of radiation of lampblack at the same temperature, is equal to unity. This is the absolute power of emission.

The absolute power of emission of the non-luminous pale-blue flame of the Bunsen burner is equal to 0.3129.

The relative power of emission of a flame is determined by multiplying the ratio between its intensity of radiation and the *maximum inten-*

sity (the intensity of radiation if the same flame were of an infinite thickness), by the absolute power of emission of the class of flame to which the one in question belongs.

The electric light emits two classes of rays, one from the incandescent carbon, which are white, the other from the voltaic arc, which are bluish-purple; these together give a bluish-white light.

The temperatures of the two carbon poles differ, and they may be calculated from the formula  $y = mT^2(T - \theta) - n(T - \theta)$ , on the supposition that the emission power of the carbon is a maximum. The power of emission of the voltaic arc is very small, like that of non-luminous flames. Its temperature may be calculated from the above formulæ, but it is necessary to introduce the value of the emission power of the arc proportional to its thickness.

Experiments show that the maximum temperature of the incandescent portion of the positive pole is about  $3,900^\circ\text{C}$ ., and that of the negative,  $3,150^\circ\text{C}$ . The temperature of the voltaic arc between the poles is always the same, about  $4,800^\circ\text{C}$ ., whatever the volume of the arc or the intensity of the current.

L. T. O'S.

**Specific Heat of Concentrated Solutions of Hydrochloric Acid.** By H. HAMMERSL (*Compt. rend.*, 89, 877—883).—The author has determined the specific heat of strong solutions of hydrogen chloride between the temperatures  $-12^\circ$  and  $+12^\circ$  with the following results:—

| HCl<br>p c. | H <sub>2</sub> O<br>for<br>1HCl. | HCl +<br>nH <sub>2</sub> O. | Sp. heat<br>by<br>heating. | Sp. heat<br>by<br>cooling. | Value in<br>water<br>for 1 cc.<br>of<br>solution. | C.<br>Molecu-<br>lar heats. | C',<br>Molecu-<br>lar heat<br>of water<br>(nH <sub>2</sub> O). | C' - C. |
|-------------|----------------------------------|-----------------------------|----------------------------|----------------------------|---|-----------------------------|--|---------|
| 32·37       | 4·23                             | 112·7                       | 0·6270                     | —                          | 0·727   | 70·70                       | 76·20  | 5·50    |
| 28·18       | 5·20                             | 130·2                       | 0·6602                     | —                          | 0·752   | 85·95                       | 93·70  | 7·75    |
| 25·37       | 5·96                             | 143·8                       | 0·6797                     | —                          | 0·765   | 97·75                       | 107·35   | 9·60    |
| 23·82       | 6·49                             | 153·3                       | 0·6868                     | 0·6895                     | 0·769   | 105·45                      | 116·80   | 11·35   |
| 18·30       | 9·05                             | 199·4                       | 0·7436                     | 0·7502                     | 0·814   | 148·95                      | 162·95   | 14·00   |
| 12·50       | 14·19                            | 291·9                       | 0·8076                     | 0·8132                     | 0·860   | 236·60                      | 255·50   | 18·90   |
| 6·53        | 29·02                            | 558·8                       | —                          | 0·8983                     | 0·925   | 501·95                      | 522·35   | 20·40   |
| 4·80        | 47·67                            | 894·5                       | —                          | 0·9310                     | 0·950   | 832·80                      | 858·10   | 25·30   |

The following formula expresses the molecular heats of strong as well as of weak solutions of HCl:—

$$C = 18n - 28·39 + \frac{151·3}{n} - \frac{242·1}{n^2} \quad \text{W. R.}$$

**Heat of Formation of Ammonia.** By BERTHELOT (*Compt. rend.*, 89, 877—883).—The heat evolved during the formation of ammonia, water, carbonic anhydride, and hydrochloric acid are among the most important data of thermo-chemistry. The last three have been frequently measured, but the heat equivalent of the formation of ammonia has been measured only twice, and the determinations are,

therefore of doubtful value. Favre and Silberman, and Thomsen have determined it by means of the reaction between chlorine and ammonia, supposing the reaction to be complete. The difference between the determinations of these independent observers is about 20 per cent. In determining the heat evolved by the action of hypobromites on urea, numbers were obtained which did not coincide with those of the former experimenters on ammonia, for by this indirect method 22.8 kil.-degrees of heat were evolved for 14 grams of nitrogen, instead of 31.5 found by Favre and Silberman, or 35.15 by Thomsen. These results are so abnormal that the author investigated the action of chlorine on ammonia, by aid of which the other experimenters had determined the heat equivalent of ammonia. He found that when chlorine is passed through a dilute solution of ammonia, considerably less than half the nitrogen equivalent to the chlorine is liberated, whilst ammonium hypochlorite, and possibly bases intermediate between ammonia and nitrogen chloride, are formed. Satisfactory results were, however, obtained by burning ammonia in oxygen, the sole products being nitrogen and water. The average of five determinations, closely concordant with one another, gave, for 17 grams of ammonia, an evolution of 91.3 kil.-degrees. Now  $(H_2 + O = H_2O \text{ liquid})$  evolves 69.0, or 34.5 for each atom of hydrogen, hence  $N + H_2 = NH_3$  (gas) evolves  $(34.5 \times 3) - 91.3 = 12.2$ , and as solution of  $NH_3$  in water evolves 8.82 kil.-degrees, the total heat of formation of  $N + H_2 +$  solution in water is 21.0 kil.-degrees. W. R.

**Relation between the Heat Developed on Solution and that Developed on Dilution, with Complex Solvents** (*Compt. rend.*, 89, 967); **Thermo-Chemistry of Cuprous Chloride** (*ibid.*, 89, 967—971). By BERTHELOT.—Let  $D$  = heat evolved by dissolving a salt in any solvent not water; and  $\Delta$  = heat evolved on dilution with water; and similarly let  $\Delta'$  be heat evolved by addition of water to the solvent, and  $D'$  the heat evolved on dissolving the substance in the dilute solvent; then  $D' - D = \Delta' - \Delta$ . For example, cuprous chloride dissolved in hydrochloric acid gives off a certain amount of heat, and on dilution, a further amount; or if the hydrochloric acid be diluted, it evolves a certain amount, and subsequent solution of cuprous chloride in it evolves a further amount: the difference between that evolved by dissolving the salt in strong acid and that evolved on dissolving in weak acid is equal to the difference between the dilution of the concentrated solution and that evolved by diluting the acid. In the second paper Berthelot gives details of this experiment. On dissolving  $Cu_2Cl_2$  in hydrochloric acid the absorption of heat increases as the dilution of the acid increases until it reaches its maximum, when the solution is no longer stable, but begins to give a precipitate. This phenomenon is the resultant of various distinct actions. 1st.  $Cu_2Cl_2$  forms a definite compound with a portion of the solvent, developing a constant amount of heat which is termed  $+A$ . 2nd. This compound dissolves, absorbing heat approximately constant if a large excess of solvent be used, termed  $-B$ . 3rd. If the relation between water and acid in the new compound differs from that of the original solvent, the definite hydrates contained in the latter undergo partial decomposi-

tion and absorb a variable quantity of heat = C. 4th. Those portions of the hydrate, decomposed by the formation of the new compound, cause liberation of water, which unites with the unsaturated hydrates of hydrochloric acid and develops heat + K; this is equal to 0 when the liquid is so dilute that saturated hydrates may be formed, and in such a case the formation of a new cuprous compound is possible only when its heat of formation is greater than that of the hydrates which it decomposes. This explains the decrease of solubility of cuprous chlorides with dilution of the solutions. Thus the resultant,  $D = A - B - C + K = (A + K) - (B + C)$ , is the algebraic sum of two positive quantities, one constant, A, and one decreasing with dilution, K; and two negative quantities, -B, almost constant if the amount of cuprous chloride is small compared to the solvent, and -C, which increases with dilution up to a certain limit. D therefore increases with dilution up to a point where the tendency of cuprous chloride to form a definite compound with the hydracid is balanced by the insolubility of the chloride. The experimental data for determining the heat of formation of  $\text{Cu}_2\text{Cl}_2$  is given in the following two tables, which themselves explain the method of determining it:—

|  |      |  |          |
|--|------|--|----------|
| $\frac{1}{2}(\text{BaO} + \text{O} = \text{BaO}_2)$ evolves .. | 6.0  | + dilute HCl .....   | 27.8     |
| H + Cl + water = HCl, dilute                                   | 89.3 | $\frac{1}{2}(\text{H}_2 + \text{O} = \text{H}_2\text{O})$ .....                | 34.5     |
| Reaction on $\frac{1}{2}\text{Cu}_2\text{Cl}_2$ .....          | 44.0 | $\frac{1}{2}\text{Cu}_2\text{Cl}_2 + \text{Cl} + \text{water} = \text{CuCl}_2$ |          |
|  |      | dissolved .....  | x        |
|  | 89.3 |  | x + 62.3 |

Hence  $x = 27.0$ . To check these results the following measurement was made:—

|   |       |  |          |
|---|-------|--|----------|
| $\frac{1}{2}(\text{H}_2\text{O} + \text{O} = \text{H}_2\text{O}_2)$ , dilute .. | -10.7 | $\frac{1}{2}(\text{H}_2 + \text{O} = \text{H}_2\text{O})$ .....                | 34.5     |
| H + Cl + water = HCl, dilute  | 89.3  | $\frac{1}{2}\text{Cu}_2\text{Cl}_2 + \text{Cl} + \text{water} = \text{CuCl}_2$ |          |
| Reaction on $\frac{1}{2}\text{Cu}_2\text{Cl}_2$ .....                           | 83.0  | dissolved .....  | x        |
|   | 61.6  |  | x + 34.5 |

Hence  $x = 27.1$ , corresponding with the former result. From former experiments it has been found that  $\frac{1}{2}(\text{Cu} + \text{Cl}_2 = \text{CuCl}_2)$  evolves 62.6 c., hence  $\frac{1}{2}(\text{Cu}_2 + \text{Cl}_2 = \text{Cu}_2\text{Cl}_2)$  anhydrous evolves 35.6.

W. R.

**The Temperature of Decomposition of Vapours.** By H. ST. CLAIRED DEVILLE (*Compt. rend.*, 89, 803—806).—This paper has special reference to the long-disputed question of the dissociation of chloral hydrate when heated. The author remarks that change of temperature cannot be taken as proof of combination or decomposition, and the observation made by Wurtz that no change of temperature accompanies the mixing of chloral vapour with vapour of water, does not prove that combination has not taken place, nor would a rise of temperature have been conclusive that combination had occurred. If two vapours, e.g., vapours of carbon bisulphide and of ether be mixed, contraction takes place and liquid may even be seen to condense. This of course is accompanied by change of temperature, yet no combination is supposed to take place.

Granting even that water-vapour and chloral vapour do not com-

bine, Wurtz's assertion that such compounds, including ammonium chloride, cannot exist in the gaseous state without decomposition is evidently incorrect; for nitrogen chloride, which absorbs 38,478 gram-degrees per equivalent during its formation should be incapable of existing in the state of vapour, yet it can be boiled; and had Troost and the author had any method of sealing the vessel in which it was contained, its vapour-density could have been determined, and, on the other hand, water, which evolves 33,500 gram-degrees, shows decomposition about  $1,000^{\circ}$ , and can be resolved into its constituents by diffusion. It is thus evident that the heat evolved by a compound during formation has no connection with the temperature of its decomposition, and that the old confusion between heat and temperature is the ground of Wurtz's objections.

W. R.

**Solubility of Solids in Gases.** By J. B. HANNAY and J. HOGARTH (*Chem. News*, 40, 256).—This investigation was undertaken in the hope that, by an examination of the conditions of liquid matter up to the "critical" point, sufficient knowledge might be gained to enable the authors to determine under what particular conditions liquids are dynamically comparable, in order that the microrheometrical method might be applied, to determine their molecular mass and energy relations. The question as to the state of matter immediately beyond the critical point being considered by Andrews to be at that time incapable of receiving an answer, the authors imagined that some insight might be gained into its condition by dissolving in the liquid some solid substance, whose fusing point was much above the critical point of the liquid, and noticing, whether, on the latter passing its critical point, and assuming the gaseous condition, the solid was precipitated or remained in solution. It was found that the solid was not deposited, but remained in solution or rather in diffusion, in the atmosphere of vapour. Experiments were made with strong gaseous solutions of solids, using as solvents alcohol, ether, carbon bisulphide and tetrachloride, paraffin and olefines, and as solids, sulphur, chlorides, bromides and iodides of the metals, and organic substances such as chlorophyll and the aniline dyes. It was found that, when the side of a tube containing a strong gaseous solution of a solid is approached by a red-hot iron, the part next the source of heat becomes coated with a crystalline deposit, which slowly redissolves on allowing the local disturbance of temperature to disappear. The authors also examined the spectroscopic appearances of solutions of solids when their liquid menstrua were passing to the gaseous state; but as all the substances they have yet been able to obtain in the two states give banded spectra with nebulous edges, the authors are only able to state that the substance does not show any appreciable change at the critical point of its solvent. It was considered to be most interesting to experiment on a body such as sodium, which besides being an element, yields in the gaseous state sharp absorption lines. It was found that on working with the blue solution of sodium in liquefied ammonia, and raising the ammonia above its critical point, the sodium combined with some constituent of the gas, forming a white solid, and yielding a permanent gas, probably hydrogen.

When the solid is precipitated by suddenly reducing the pressure it is crystalline, and may be brought down as a "snow" in the gas, or on the glass as a "frost," but it is always easily redissolved by the gas on increasing the pressure.

The above, therefore, is the phenomenon of a solid with no measurable gaseous pressure dissolving in a gas, and not being affected by the passage of its menstruum through the critical point to the liquid state, showing it to be a true case of gaseous solution of a solid.

D. B.

**Tension of the Vapours of Saline Solutions.** By E. PAUGHON (*Compt. rend.*, 89, 752—754).—In examining certain thermodynamic formulæ, particularly those of Kirchhoff, the author has found it necessary to determine the vapour-tension of different saline solutions between the temperatures of 0 and 50°. The method employed was that of Regnault, with slight modifications. An ordinary barometer is placed between two others, one containing the solution, the other water. Up to 30—35° the parabolic relations represent the results very exactly, but above that temperature irregularities occur, which increase rapidly with the temperature, the diminution in the elastic force being always less than that given by the empirical formula. Kirchhoff's formula for low temperatures is of the form  $d = a\phi + b\phi^2$ , in which  $d$  = the diminution of tension referred to the unit weight of salt dissolved in 100 parts of water,  $\phi$  = maximum tension of aqueous vapour at the same temperature,  $a$  and  $b$  certain coefficients determined by experiments, which are given for certain salts. These coefficients are found in some cases to increase, and others to decrease with the weight of salt. To find the formula for any solution containing a given weight of salt  $\pi$ , let  $\alpha$  and  $\beta$  be the constants to be determined, and let  $a$  and  $b$ ,  $a'$  and  $b'$ , be the coefficients of two solutions containing weights  $P$  and  $P'$  of the same salt given in the table, of which  $P < \pi$  and  $P' > \pi$ , then if  $P' = \pi + p$  we have—

$$\alpha = a + (a' - a) \frac{p}{P' - P}, \text{ and}$$

$$\beta = b + (b' - b) \frac{p}{P' - P}.$$

All things being equal, the diminution of tension is not strictly proportional to the quantity of salt dissolved.

L. T. O'S.

**Passive State of Iron.** By L. VARENNE (*Compt. rend.*, 89, 783—786).—From a series of experiments, the author concludes that the passive state of iron is due to the formation of a gaseous envelope, which surrounds the surface of the metal when plunged into strong nitric acid. He shows that the action of dilute nitric acid on iron in the passive state may be established not only by rubbing the surface of the metal, but also by setting up a series of vibrations or by causing a current of gas to come in contact with the metal. A piece of iron rendered passive, after being placed in a vacuum, is readily attacked by dilute nitric acid. The gas which envelopes the metal is nitric oxide.

L. T. O'S.

**Relation of the Volumes of Solutions of Hydrated Salts to their Water of Composition.** By R. J. SOUTHWORTH (*Am. J. Sci.* [3], 17, 399—401).—The author has tested by experiment the following theorem:—If a hydrated salt be dissolved in a given volume of water, the volume of the solution will exceed the original volume of the water by a bulk equal to the bulk of saline water contained in the salt dissolved. The expression *saline water* is used to mean all the water contained in the salt, both water of crystallisation and water of constitution. The results of the experiments are exhibited in the following table. The first column of numbers gives the weight of each salt tried which contains 1 c.c. of saline water, calculated from the formula. The second column gives the weight of each salt, which was found necessary to increase the volume of the solution by 1 c.c. The calculated numbers agree closely with the experimental ones in all instances except barium chloride and sodium hydrogen sulphate, thus proving the general truth of the proposition.

| Salt used.  | Calculation. | Experiment. |
|---|--------------|-------------|
| $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .....                                     | 1.588 grams  | 1.59 grams  |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .....                                     | 1.788 "      | 1.63 "      |
| $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ .....          | 4.083 "      | 3.25 "      |
| $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .....                            | 2.122 "      | 2.12 "      |
| $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .....                                    | 1.591 "      | 1.59 "      |
| $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .....   | 6.777 "      | 3.89 "      |
| $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ .....   | 2.468 "      | 2.47 "      |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .....   | 1.954 "      | 1.95 "      |
| $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .....   | 2.277 "      | 2.28 "      |
| $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .....   | 2.228 "      | 2.23 "      |
| $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .....   | 2.206 "      | 2.20 "      |
| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .....   | 2.771 "      | 2.77 "      |
| $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .....                                 | 2.058 "      | 2.06 "      |
| $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ....      | 2.196 "      | 2.20 "      |
| $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ .... | 2.099 "      | 2.10 "      |
| $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ....      | 2.31 "       | 2.31 "      |
|   |              | J. M. H. M. |

**Six Lecture Experiments.** By O. v. THAN (*Ber.*, 12, 1411—1416).—(1.) The conductivity of hydrogen for heat may be shown by rendering incandescent, by a current of suitable strength, a fine platinum wire which joins the upper and out-bent extremities of two stout copper wires fixed parallel and vertically in a cork by means of glass tubes. The glow of the wire disappears on inverting over it a cylinder of hydrogen, while the gas burns at the mouth.

(2.) By interposing short bars of different metals in the circuit, the difference in their conducting powers will be shown by the more or less lively glow of the platinum wire.

(3.) A jet of oxygen may be burnt in a two-necked glass balloon containing sulphur, which is vaporised by the heat of a Bunsen. The gas is best kindled by means of a morsel of charcoal fastened to the end of the jet. This is ignited before introducing the jet into the balloon.

(4.) The indestructibility of matter may be demonstrated by preparing two sealed glass tubes of equal weight, one of them containing

oxygen and a little powdered charcoal. The charcoal may be caused to burn away completely by heating it by means of a small flame; on placing the two tubes on a balance it will be seen that there has been no variation in weight.

(5.) The usual experiments for illustrating the laws of diffusion of gases through porous plates, are apt to convey to the minds of beginners false ideas as to the rate at which one gas propagates itself through another by diffusion alone. That this is extremely slow, owing to the numerous collisions between the molecules, may be proved by suspending a slip of paper, moistened with lead solution, from the bottom of a tall inverted cylinder into which the stopper is inserted. In the hollow of the latter a little hydrogen sulphide solution is placed. Blackening of the lead-paper does not occur for ten to fifteen minutes. Chlorine water and potassium iodide paper may also be used.

(6.) The diffusion of gases through colloid membranes may be demonstrated by fastening a piece of thin india-rubber (from a toy balloon) over the mouth of a funnel, which is then placed in an inverted bell-jar. The stem of the funnel is connected (best by a side tube) with a U-tube containing a little mercury. If the bell-jar be filled with carbonic anhydride, there will be increased tension within the funnel, and therefore a rise in the mercury. If one terminal of a voltaic circuit including an electric-bell be plunged into the mercury, matters may be so arranged that the mercury in rising shall come in contact with the other, a fact announced by the ringing of the bell.

The paper is illustrated by diagrams.

Ch. B.

## Inorganic Chemistry.

**Non-production of Ozone in the Crystallisation of Iodic Acid.** By A. R. LEEDS (*Chem. News*, 40, 257).—It has been stated by Croft that air over crystallising iodic acid becomes ozonised. The author has repeated Croft's experiments, and explains this reaction quite differently. When the difficulty of getting rid of every trace of extraneous matter by chemical operations—however carefully conducted—is borne in mind, it appears to the author that the simplest explanation of the apparent ozonic reaction is that the phenomenon is not due to ozone produced in the act of crystallising—which, as Croft remarks, is anomalous—but to a trace of chlorine or nitrous acid, or possibly some lower oxide of iodine formed in the process of manufacture, and eliminated by successive crystallisations of the acid. After washing, the air did not manifest the ozone reaction, a fact which strongly corroborates this view.

D. B.

**Solubility of Ozone in Water.** By A. R. LEEDS (*Ber.*, 12, 1831—1834).—The author concludes that ozone is soluble in water, for when strips of paper are moistened with lead acetate, the latter converted



into sulphide, and the strips fastened under a layer of water 1 cm. deep, and then exposed for several hours to a current of air containing ozone, oxidation takes place, lead peroxide and sulphuric acid being formed. Bright silver foil similarly treated also shows evidence of the action of ozone.

P. P. B.

**Behaviour of Chlorine at High Temperatures.** By V. MEYER and C. MEYER (*Ber.*, 12, 1426—1431).—In order to meet the objection that might be advanced against their method of determining vapour-densities at very high temperatures, viz., that the molecules of the nitrogen gas in which the substance is volatilised might themselves undergo dissociation, the authors have made several determinations of the density of mercury vapour at 440 and 1,567°. According to current theories the molecules of that metal consist of single atoms. Agreement between the determinations of its density at the above two temperatures would therefore show that nitrogen gas is not itself dissociated at the higher one. Experiment gave, for mercury at 440° density = 6.86, at 1,567° density = 6.81. Theoretical for Hg = 6.91.

The following determinations of the sp. gr. of oxygen were made:—Oxygen was weighed and introduced into the apparatus in the form of silver oxide, previous experiments having shown that silver gives off no appreciable vapour at the highest temperature reached. At 1,392° = 1.06 and 1.04; at 1,567° = 1.04 and 1.10. Theoretical for O<sub>2</sub> = 1.05.

In determining the density of chlorine most remarkable results were arrived at. Chlorine was weighed and introduced in the form of platinous chloride, a salt easily prepared, and having the great advantage over other easily decomposable chlorides of not being deliquescent. It was found that up to about 620° the density of chlorine is constant, corresponding with the molecular formula Cl<sub>2</sub>. A little above this temperature dissociation commences, and at 800 and 1,000° intermediate numbers are obtained. Above 1,200° the density again becomes constant, the molecular weight being exactly  $\frac{3}{2}$  Cl<sub>2</sub>. The following are the actual numbers observed:—

|                         |                           |
|-------------------------|---------------------------|
| At 620° = 2.42 and 2.46 | At 1,242° = 1.65 and 1.66 |
| „ 808 = 2.21 „ 2.19     | „ 1,392 = 1.66 „ 1.67     |
| „ 1,028 = 1.85 „ 1.89   | „ 1,567 = 1.6 „ 1.63      |

Theoretical for Cl<sub>2</sub> = 2.45; for  $\frac{3}{2}$  Cl<sub>2</sub> = 1.63.

The molecular weight of chlorine, which at low temperatures = 71, becomes therefore at high temperatures = 47.3.

That the walls of the porcelain vessel were not attacked during the experiment was proved by exposing a piece of porcelain at about 1567° to a current of dry chlorine for an hour and a half, after which not the least change in its weight could be detected.

The authors postpone discussion of their results until experiments with iodine and bromine have been completed. Already they have ascertained that iodine at high temperatures behaves like chlorine; a fact of great importance, since it renders necessary a revision of the determinations of Deville and Troost, in which the constancy of the density of iodine vapour is assumed. In order to test the truth of the

old Murium theory, in which chlorine is regarded as an oxide, they purpose causing dissociated chlorine to diffuse through a porous diaphragm. Ch. B.

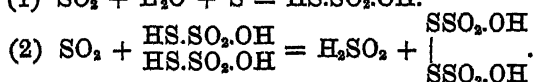
**Solidifying Point of Bromine.** By J. PHILIPP (*Ber.*, 12, 1424).—Pure bromine solidifies at  $-7.2$  to  $-7.3^{\circ}$ . This determination agrees well with that of Regnault ( $-7.32^{\circ}$ ) and that of Pierre ( $-7.5$  to  $-7.8^{\circ}$ ), but differs much from those of other chemists. The melting point is slightly raised by addition of iodine, but considerably lowered by the presence of chlorine. Solid bromine is brown in colour, and has a conchoidal fracture. Exposure to air (moisture?) gives it a grey colour and crystalline appearance. Ch. B.

**Non-existence of Pentathionic Acid.** By W. SPRING (*Annalen*, 199, 97—115).—After referring to the researches of Wackenroder (*Ann. Chim. Phys.* [3], 20, 144, and *Annalen*, 60, 189), Fordos and Gélis (*Ann. Chim. Phys.* [3], 22, 66, and *Annalen*, 64, 249), Kessler (*Annalen*, 68, 233), and Risler-Bennat (*Pogg. Ann.*, 116, 470) on pentathionic acid, the author describes his attempts to prepare this acid.

When sulphuretted hydrogen and sulphurous anhydride are simultaneously passed into water, finely divided sulphur separates out (which may be removed by the addition of freshly precipitated metallic copper), and an acid remains in solution which Wackenroder believed to be pentathionic acid. The acid liquid is concentrated to 1.30 sp. gr. and extracted with ether. On the addition of a dilute aqueous solution of potassium carbonate to the ethereal solution mixed with alcohol a white precipitate of *potassium tetrathionate* is obtained. If the aqueous solution of the acid is neutralised with potash or baryta, the salt which is produced invariably contains free sulphur. This explains the fact that Wackenroder found the relation between the atoms of sulphur and potassium to be greater than 4 to 2.

Kessler distinguished *penta-* from *tetra-*thionic acid by the ammonium salt of the former producing with sulphuretted hydrogen a precipitate of sulphur, and with silver nitrate a precipitate of silver sulphide. These reactions are, however, also exhibited by ammonium tetrathionate, but not by barium tetrathionate. The precipitate which is deposited by a solution of barium tetrathionate does not consist of pure sulphur, as was formerly supposed, but contains almost half its weight of barium sulphate and sulphite.

The reaction which really takes place when sulphuretted hydrogen and sulphurous anhydride act on each other in presence of water, is the formation of thiosulphuric acid and the oxidation of this acid to tetrathionic by the excess of sulphurous anhydride:—



The presence of hyposulphurous acid,  $\text{H}_2\text{SO}_2$ , can be detected by its property of bleaching indigo both in acid and in alkaline solutions.

Fordos and Gélis's method of acting on sulphurous acid with sulphur dichloride, and neutralising the product with freshly precipitated barium carbonate also yields barium tetrathionate and not the pentathionate. W. C. W.

**Action of Lime on Silica in Mortar.** By W. B. ROBERTS (*Chem. News*, 40, 250).—Having found in the recent analysis of some specimens of old mortar from the walls of a building erected about 200 years ago, considerable traces of hydrated silica, it occurred to the author that possibly the hardening or setting of mortar might be due to some chemical action occurring between the lime and the silica when these ingredients were mixed, whereby some proportion of the silica was caused to assume the gelatinous form; that this being then incorporated by the usual mixing process, subsequently solidified, binding the whole bulk with a hard network of silica. Experiments were made to test this point, and the author's general conclusions may be summarised as follows:—

(1.) Practically no gelatinisation of silica occurs in the manufacture of mortar.

(2.) Under the ordinary conditions of access of air the lime in mortars becomes gradually dehydrated, absorbs carbonic acid, and forms neutral carbonate.

(3.) The absorption of carbonic acid is very slow.

(4.) A slight action takes place between the lime and the silica, although very small.

(5.) Although even the small proportion of dry silicates slightly increases the hardness of a mortar, the ordinarily sufficient hardness of mortar is obtained by simple dehydration and carbonation.

These conclusions appear to be confirmed by the fact that lime already containing a small proportion of carbonate is preferred to pure lime for making mortar. D. B.

**Arsenates of Zinc and Cadmium.** By H. SALKOWSKI (*Ber.*, 12, 1446—1449).—Arsenates of the form  $5R''O, 2As_2O_5 + nH_2O$ , were long since prepared by the author (*J. pr. Chem.*, 104, 109).—The only similar compound occurring in nature is perhaps *picroparmacolite*,  $5(Ca.Mg)O.2As_2O_5 + 12H_2O$ , corresponding with the natural phosphates, *hureanlite* and *heterosite*,  $5(Mn.Fe)O, 2P_2O_5 + 5H_2O$ , and the artificial phosphates,  $5MnO.2P_2O_5 + 5H_2O$  (Erlenmeyer and Heinrich, *Annalen*, 190, 195) and  $5ZnO.2P_2O_5 + 5H_2O$  (Demol, *Ber.*, 12, 1174). Quite recently Demol (*Ber.*, 12, 1279) has described the arsenates,  $5ZnO.2As_2O_5 + 5H_2O$ , and  $5CdO.2As_2O_5 + 5H_2O$ , already prepared by the author, although in a different way (*loc. cit.*). In addition to these Demol has described the salt  $AsO_4.HZn + H_2O$ . This salt the author had also prepared by a different method, viz., by allowing common zinc arsenate to remain for more than a year in contact with a solution of arsenic acid. The deposit, after washing with cold water and drying at  $120^\circ$ , consisted of the above salt; and by evaporating the filtrate, allowing the residue to deliquesce, washing it with cold water and alcohol, and boiling it with water, a second arsenate, probably  $Zn(AsO_3)_2$ , was obtained as a heavy white powder.

Setterberg by evaporating solutions of arsenates in arsenic acid and

heating the residues, has obtained arsenates,  $\text{BaO} \cdot 2\text{As}_2\text{O}_5 + 4\text{H}_2\text{O}$  and  $\text{Ag}_2\text{O} \cdot \text{As}_2\text{O}_5 + 2\text{H}_2\text{O}$ , analogous to Maddrell's metaphosphates. Hurtzig and Geuther (*Annalen*, 111, 168) obtained by the same method the salt  $\text{Ag}_2\text{O} \cdot \text{As}_2\text{O}_5$ . Both silver salts were decomposed by water. By dissolving various compounds; oxides (Mn), chlorides (Ba, Sr, Ca, Cd, Cu), nitrates (Ag), and arsenates (Zn, Cd, Cu, Ag) in arsenic acid, evaporating, heating the residue for some time at  $200^\circ$ , and washing with water and alcohol, the author claims to have prepared the following in addition:—Of the form  $\text{R}'\text{O} \cdot \text{As}_2\text{O}_5$ , salts in which  $\text{R}' = \text{Sr, Ca, Zn, Cd, or Ag}$ ; also  $\text{BaO} \cdot 2\text{As}_2\text{O}_5$  and  $2\text{CuO} \cdot \text{As}_2\text{O}_5$ . Only the silver salt was washed with dilute nitric acid. All these salts are either sparingly soluble, or quite insoluble, in water. No peculiar modification of arsenic acid could be detected in them.

The analyses are mostly very unsatisfactory.

Ch. B.

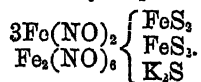
**Arsenates of Zinc and Cadmium.** By W. DEMEL (*Ber.*, 12, 1949).—A reply to Salkowsky (*Ber.*, 12, 1446) as to priority of discovery.

**Ultramarine Compounds.** By K. HEUMANN (*Annalen*, 199, 253—281).—That portion of the paper which refers to the mode of preparation and to the properties of silver ultramarine has appeared in the *Berichte* (10, 991, 1345, 1888, and 12, '60) and in this Journal (1877, 2, 572, 707; 1878, Abst., 113; 1879, Abst., 437).—By the action of the alkaline haloids and of methyl and ethyl iodides on silver ultramarine, the silver is replaced more or less completely. When silver ultramarine is heated in a current of chlorine gas or iodine vapour, a flesh-coloured mass is formed which yields green ultramarine on fusion with potassium iodide. Heated to redness in an atmosphere of hydrogen, silver ultramarine blackens and evolves a small quantity of sulphuretted hydrogen. The ultramarine is completely decomposed by the action of sulphuretted hydrogen.

W. C. W.

**Roussin's Salt.** By O. PAWEL (*Ber.*, 12, 1407—1411).—The salt named *dinitrosulphide of iron* by Roussin has been investigated by Porczynsky (*Annalen*, 125, 302), Rosenberg, and recently by Demel (*Ber.*, 12, 461), but with widely discrepant results. Roussin's method of preparation gives it in a very impure form; the following is therefore recommended by the author:—A solution of 80 grams of potassium nitrite (50 per cent.) in 300 c.c. of boiling water, is mixed with a cold solution of 80 grams of sodium sulphide in 300 c.c. of water. 70 grams of ferrous sulphate dissolved in 300 c.c. of water is gradually added to the mixture with constant shaking, the whole heated on a water-bath for half an hour at  $70-80^\circ$ , and filtered. After forty-eight hours the salt is deposited from the filtrate. The neutral potassium sulphide, or the hydrosulphide of potassium, sodium, calcium or barium, may be used as a substitute for the sodium sulphide. The salt may also be prepared by adding a dilute solution of potassium hydrosulphide to a very dilute solution of nitric oxide in ferrous sulphate, and slowly warming. The impure black crystals from either operation must be recrystallised from warm water, air-dried, and dissolved

in ether. The dried and powdered residue from the evaporated ethereal filtrate is digested with pure carbon bisulphide, and after washing with chloroform recrystallised from warm water, to which a few drops of potash solution have been added. The crystals, which are hard, brilliant, monoclinic prisms, are not affected by sunlight, and but little by exposure to air. Analysis leads to the formula,  $\text{Fe}_7\text{S}_8(\text{NO})_{12}\text{K}_2 + 2\text{H}_2\text{O}$ , which may be put in the rational form—



When ammonium sulphide is used in its preparation, as by Roussin, Rosenberg and Demel, the product contains both potassium and ammonium: hence the discrepancies between the results of those chemists. The potassium and ammonium salts resemble each other closely; but the former, being more soluble than the latter, may be completely converted into it by digestion with ammonium carbonate. The sodium salt is easily soluble, and is identical with the iron nitrosulphocarbonate of Löw (*Chem. Centr.*, 1865, 948). Ch. B.

**Roussin's Salt.** By O. PAWEŁ (*Ber.*, 12, 1949—1956).—It has been previously shown (see previous abstract) that the compound described as nitroso-ferrous sulphide is a mixture of several salts with sulphur, and that it always contains an alkali-metal. The author in the present communication describes methods for preparing the potassium, sodium, ammonium, ferrous, and other salts of the above compound. These have the general formula,  $\text{Fe}_7\text{S}_8(\text{NO})_{12}\text{M}_2 + 2\text{H}_2\text{O}$ , except that the ferrous salt crystallises with 8 instead of 2 mols. of water.

The ammonium salt is less soluble in water than the potassium salt, and like the latter crystallises in brilliant monoclinic crystals, which dissolve in water with a light brown colour: it begins to decompose at 80°. Of all these salts, the potassium and ammonium compounds are the most stable.

The so-called nitroso-sodio-ferrous sulphide was also prepared and investigated. It is best obtained by heating the ammonium salt above referred to on a water-bath with soda, until ammonia is no longer evolved. It forms dark-red crystals, which are insoluble in ether but soluble in alcohol and water, giving a neutral solution. It begins to decompose on heating at 115°, and gradually at the ordinary temperature on exposure to the air (on account of the carbonic acid present), after which the aqueous solution becomes alkaline; in all these cases, the sodium salt first referred to is formed with evolution of sulphuretted hydrogen.

The paper concludes with theoretical considerations as to the constitution of these various compounds. T. C.

**Roussin's Salt.** By W. DEMEL (*Ber.*, 12, 1948).—This is merely a reply to Paweł's remarks (*ibid.*, 1410) on the paper by Roussin, Rosenberg, and Demel (*ibid.*, 461) concerning the salt prepared by them from ferrous sulphate, potassium nitrite, and ammonium sulphide. T. C.

**Composition of the Weldon Manganese "Mud" and some Similar Compounds.** By J. Post (*Ber.*, 12, 1454—1459).—According to Weldon, the manganese dioxide obtained in his regenerative process exists in combination with lime as  $\text{CaO} \cdot \text{MnO}_2$ , or  $\text{CaO}(\text{MnO}_2)_2$ . Gorgeu too (*Ann. Chim. Phys.* [3], 66, 153) has described a "*manganous acid*" (manganese dioxide), which he formed by repeated treatment of the red oxide with boiling concentrated nitric acid. This acid was said to redden litmus, to dissolve lime and baryta, and to decompose carbonates. Various neutral salts were rendered acid by the addition of "*manganous acid*," and Gorgeu even described some of its salts, such as  $(\text{MnO}_2)_2\text{MnO}$ ,  $(\text{MnO}_2)_2\text{CaO}$ ,  $(\text{MnO}_2)_2\text{K}_2\text{O}$ .

By careful analysis of some of these compounds, the author shows the theories of Weldon and Gorgeu to be incorrect. The composition of the Weldon mud is not such as to lead to the conclusion that it contains a definite compound of lime and manganese dioxide; and in the so-called salts of Gorgeu, he has not found so much as half the amount of base stated by that chemist to be contained in them. They are rather to be regarded as mixtures of manganese dioxide with various compounds. Tables of analytical results are given.

Ch. B.

**Behaviour of Bismuth containing Arsenic towards Nitric Acid, and the Preparation of Basic Bismuth Nitrate, free from Arsenic.** By R. SCHNEIDER (*J. pr. Chem.*, 20, 418—434).—Many varieties of commercial bismuth contain a small quantity of arsenic, and in the ordinary process of preparing officinal bismuth sub-nitrate, the arsenic is incompletely eliminated. In dissolving metallic bismuth by aid of heat in strong nitric acid, the arsenic present is oxidised to arsenic acid, and combines with bismuth, forming bismuth arsenate, which is insoluble in a strong solution of bismuth nitrate, although more soluble in water. To oxidise the arsenic to arsenic acid, excess of acid must be employed, otherwise the oxidation is incomplete, and the arsenite of bismuth formed is not insoluble. The author therefore recommends that 2 kilos. of bismuth should be treated with 10 kilos. of *hot* nitric acid, and after solution, decanted from the sediment containing arsenic. On evaporation, the crystals of bismuth nitrate which separate are quite free from arsenic.

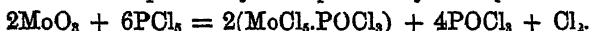
W. R.

**Vapour-density of Stannous Chloride.** By T. CARNELLEY (*Ber.*, 12, 1836—1837).—From the determinations of the vapour-density of stannous chloride (*Ber.*, 12, 1195), V. and C. Meyer attribute to it the molecular formula  $\text{Sn}_2\text{Cl}_4$ . This the author shows is due to the temperature at which the determination was made, being too near the boiling point of stannous chloride ( $617-628^\circ$ ), as determined by Carleton-Williams and himself (this Journal, Trans., 1879, 563). This is probably the cause of the low numbers obtained by Rieth (*Ber.*, 3, 668), and not that the temperature had produced decomposition.

P. P. B.

**Action of Phosphorus Pentachloride on Molybdic Anhydride.** By A. PIETRI (*Gazzetta*, 9, 538—543). As Teclé (*Annalen*, 188, 255) had obtained tungsten hexchloride by the action of phos-

phorus pentachloride on tungstic anhydride, according to the equation  $\text{WO}_3 + 3\text{PCl}_5 = \text{WCl}_6 + 3\text{POCl}_3$ , the author thought it probable that molybdenum hexchloride might be obtained in the same way. Accordingly, a mixture of molybdic anhydride (1 mol.) with phosphorus pentachloride (3 mols.) was heated in a sealed tube at  $180^\circ$  for about 5 hours. On cooling, the tube contained a reddish-brown liquid, and crystals of a dark green colour with metallic reflex. As these crystals were rapidly disintegrated on exposure to moist air, and became covered with a film of blue oxide, it was necessary to pour off the liquid in an atmosphere of dry carbonic anhydride, and subsequently to dry the crystals in a current of the same gas; this was done without removing the crystals from the tube. When the whole of the liquid had been removed, the crystals were transferred to tubes also filled with carbonic anhydride, which were at once closed before the lamp. On analysis, the substance was found to contain molybdenum, phosphorus, and chlorine in proportions corresponding with the formula,  $\text{MoCl}_5 \cdot \text{POCl}_3$ , so that it is a combination of molybdenum pentachloride and phosphorus oxychloride. It is soluble in carbon bisulphide and phosphorus oxychloride, but insoluble in chloroform, ether, and benzene. When heated, it melts at  $125$ — $127^\circ$ , and at  $170^\circ$  it enters into ebullition, and is decomposed, phosphorus oxychloride distilling over. When all the oxychloride has passed off and the residue is exposed to a higher temperature, magnificent black needles with metallic reflex sublime; these on analysis were found to be molybdenum pentachloride,  $\text{MoCl}_5$ . They melt at  $170$ — $175^\circ$  (Debray,  $185^\circ$ ). The liquid formed at the same time as the compound,  $\text{MoCl}_5 \cdot \text{POCl}_3$ , was found to be phosphorus oxychloride containing chlorine in solution, so that the reaction which takes place may be expressed by the equation—



C. E. G.

## Mineralogical Chemistry.

**Explosion in a Coal Mine due to Carbonic Anhydride.** By DULESSE (*Compt. rend.*, 89, 814—817).—On the 28th of July last, an explosion took place in a coal mine at Rochebelle (Gard) at a depth of 345 meters. There was no fire-damp in the mine, and no flame was produced by the explosion, but the mine was afterwards filled with choke-damp. The author accounts for it by supposing that the sulphur of the iron pyrites contained in the coal, or existing in its neighbourhood, becoming oxidised to sulphuric acid, had attacked some layers of limestone beneath the coal, and the generated carbonic anhydride had found vent in the mine, producing the explosion.

W. R.

**Analysis of Tetrahedrite from Huallanca, Peru.** By W. J. COMSTOCK (*Am. J. Sci.* [3], 17, 401).—The mineral caves of Huallanca are situated upon the eastern flank of the Peruvian Andes, at a height of

14,700 feet above the sea. The ores average 800 ounces of silver to the ton. The walls of the cavities are studded with crystals of tetrahedrite, some of which are two inches long. A portion of one crystal (sp. gr. 4.7) gave the following results:—

| Sulphur. |       |       | Atomic ratio.      |       |
|----------|-------|-------|--------------------|-------|
| S .....  | 26.74 | —     | S ....             | .8356 |
| Sb ..... | 9.06  | 3.56  | Sb ...             | .0748 |
| As ..... | 13.49 | 8.57  | As ...             | .1785 |
| Ag ..... | 3.86  | 0.57  | Ag <sub>2</sub> .. | .0179 |
| Cu ..... | 39.09 | 9.87  | Cu ...             | .3083 |
| Fe ..... | 5.46  | 3.12  | Fe ...             | .0975 |
| Zn ..... | 2.14  | 1.06  | Zn ...             | .0330 |
| <hr/>    |       |       |                    |       |
| 99.84    |       | 26.75 |                    |       |

From these numbers is deduced the ratio—



J. M. H. M.

**Genesis of Cinnabar Deposits.** By S. B. CHRISTY (*Am. J. Sci.* [3], 17, 453—463).—The ores of mercury have been generally regarded as formed by sublimation. The author, however, considers that the facts already known and the results of his own experiments favour the theory that cinnabar has been deposited from solutions of alkaline carbonates containing alkaline sulphides.

The following are the chief reasons adduced by the author in support of this theory:—

Cinnabar deposits are almost always found in metamorphic instead of in igneous rocks, and in immediate proximity to such substances as earthy carbonates, quartz, and bitumen, the presence of which cannot be explained on the sublimation hypothesis. On the other hand, the minerals which are associated with cinnabar in the ore-stuff—blende, galena, fahlore, iron pyrites, horn quicksilver, quartz, heavy spar, dolomite, spathic iron, gypsum, calcspar, and magnetic iron pyrites—have all, excepting the last, been produced in the wet way by various experimenters. Cinnabar volatilises only at just below a red heat (500° C.) at ordinary pressures. Assuming the temperature of the earth to increase 1° C. for every 100 feet in depth, it would take a depth of nearly 50,000 feet to give this temperature. At New Almaden, therefore, where the cinnabar crops out on the summit of a hill, we should have to assume an erosion of nearly nine miles and a-half of strata. Moreover, at such a depth the enormous pressure of superincumbent strata would greatly raise the temperature of sublimation. Pfaff, for example, has shown that the increase of temperature due to internal heat can at no depth be great enough to convert water into steam. The cinnabar deposits themselves do not usually show the signs of true fissure veins, but are found irregularly disseminated in layers and impregnations. Mercury has been recognised as a constituent (although in very minute quantity) of at least one mineral water, that of the spring "du Rocher," St. Nectaire-le-haut, Puy-de-Dôme. It is well known that mercuric sulphide is soluble in solutions



of alkaline sulphides containing free alkali, and is reprecipitated when the solution is saturated with carbonic anhydride or sulphuretted hydrogen. When mercuric sulphide is slowly deposited from such solutions, cinnabar is formed, but when rapidly deposited, as by dilution, the black or amorphous modification is produced; moreover, the black sulphide is changed into cinnabar by being heated with alkaline polysulphides. As free alkali is not known to exist in any natural mineral waters, the question still remains, from what solution has the cinnabar been deposited? It occurred to the author that mercuric sulphide, although insoluble in alkaline sulphides under ordinary conditions in the absence of free alkali, might dissolve under pressure. Some black amorphous mercuric sulphide, heated in a sealed tube with a solution of potassium-hydrogen sulphide at  $180^{\circ}$  for five hours, at a pressure of 180 lbs. to the square inch, was changed into a coherent mass of cinnabar crystals, recognisable by the naked eye, and closely resembling the crystals of native cinnabar. Similar experiments were made with other solutions, with the following results:—Solutions of sodium bicarbonate did not change the amorphous sulphide to cinnabar; solutions of water-glass were equally powerless; but when sulphuretted hydrogen was passed through either of these solutions and the tubes were again heated in the digester, the transformation was complete. Polysulphide of potassium effected the change very rapidly and completely. The presence of carbonic acid seemed to retard the formation without being able to prevent it. In all cases when the transformation had taken place, the liquid would stain the skin deep black, as is usual when mercuric sulphide is dissolved in alkaline sulphides. Finally, the experiment was tried of heating mercuric sulphide with the New Almaden Vichy water, which contains considerable quantities of sodium bicarbonate and free carbonic acid. Sulphuretted hydrogen was passed into this water, and some black mercuric sulphide heated in the solution both at ordinary pressure and in the digester (pressure 140–150 lbs., temperature  $180^{\circ}$  C.). The sulphide, which was treated in the open air, was unchanged even when examined with the microscope, whilst that treated in the digester was brownish-red even to the naked eye, and when examined under the microscope proved to be in great part changed into crystals of cinnabar.

J. M. H. M.

**Emplectite.** By F. R. W. DAW (*Chem. News*, 40, 225).—The author has recently discovered this mineral at the Aamdal copper mines in Norway. It gives on analysis:—

| Bi.   | Cu.   | Ag.  | Pb.     | S.    | SiO <sub>2</sub> . |
|-------|-------|------|---------|-------|--------------------|
| 57.72 | 17.23 | 2.91 | a trace | 19.20 | 1.30 = 98.36       |

The formula of this mineral would be  $\text{CuS} + \text{Bi}_2\text{S}_3$ . D. B.

**Artificial Laurite, and Platiniferous Iron.** By H. ST. CLAIRE DEVILLE and H. DEBRAY (*Compt. rend.*, 89, 587–592).—Wöhler, a few years ago, succeeded in isolating a new mineral which he termed *laurite*, from the osmiridium of the platiniferous sands of Borneo; this mineral, which eventually proved to be ruthenium sulphide, was,

like osmiridium itself, insoluble in *aqua regia*. The authors have succeeded in preparing laurite artificially. A mixture of ruthenium and iron pyrites with a little borax is heated to bright redness during 8 or 10 hours; the ruthenium is converted into sulphide, and dissolved by the molten ferrous sulphide. On treating the latter after cooling with hydrochloric acid, a mixture of the two sulphides of ruthenium is left undissolved: the one occurs as a black powder, soluble in nitric acid, with conversion into ruthenium sulphate; the other, crystallised in cubes or regular octohedrons, has the metallic lustre and bluish colour of laurite; it is insoluble in all acids and in *aqua regia*.

Its analysis gave Ru = 63.0, S = 37.0 per cent.; the formula RuS<sub>2</sub> requiring Ru = 61.9, S = 38.1 per cent.

By igniting this sulphide in an earthen crucible to a temperature at which the crucible begins to soften, it is decomposed, with formation of crystallised metallic ruthenium.

*Platinum Sulphide*.—Platinum melted with ten times its weight of pyrites and its own weight of borax, is converted into a sulphide which may be extracted from the ferrous sulphide by treatment with acids. It is of a grey colour, crystallised in needles, and wholly insoluble in *aqua regia*. It corresponds in composition with the monosulphide PtS, and not with the bisulphide as is the case with ruthenium.

The foregoing mixture of platinum and iron sulphides when very strongly heated leaves, after the action of acids, a crystalline metallic substance, which is platinum containing about 11 per cent. of iron. This alloy, which resembles certain natural specimens of platiniferous iron both in percentage of iron and in many other characteristics, is soluble only in *aqua regia*, and is so feebly magnetic, that it is only under the influence of a powerful electro-magnet that its magnetism can be detected at all.

The absence of magnetic properties in native platiniferous iron was noticed by Berzelius, and it is now well known that ferromanganese containing 30 per cent. of iron has no appreciable action on the magnet. Artificial alloys of platinum containing as much as 17 to 20 per cent. of iron are, however, strongly magnetic, so that experiments are still wanting in order to determine the precise relations existing between the magnetic intensity of the alloy, and the percentage of iron it may contain.

J. W.

**Artificial Production of Oligist.** By M. COPPOLA (*Gazzetta*, 9, 452—455).—When the vapour of water and of sodium chloride is allowed to act slowly on pieces of Vesuvian lava at a very high temperature, the author has found that the surface becomes covered with hæmatite, and that in some cases crystals of oligist are formed. The most favourable conditions for the production of the latter are attained when a small platinum crucible containing sodium chloride is placed at the bottom of a large earthen one, and covered with pieces of the lava. The crucible is then intensely heated for several days, whilst water is allowed to drop in slowly: under these circumstances, minute crystals of oligist are formed on the lava, and especially on those pieces which are most exposed to the action of the sodium chloride vapour.

C. E. G.

**The Mica Group.** By C. RAMMELSBERG (*Ann. Phys. Chem.* [2], 9, 113—146).—This paper is the first instalment of a monograph on the group of silicates distinguished as micas, the author's purpose being to embody the knowledge of the chemistry of micas which has been acquired since the publication of his *Handbuch der Mineralchemie* in 1875. He considers that, in the classification of micas, the proper ground of division is to be found, not in their crystalline forms or optical properties, but in their chemical constitution. From this point of view the micas may be permanently divided into two great groups:—

1. Micas which consist of silicates of aluminium and of univalent metals (to which last must also be added hydrogen). These are called the alkali-micas.

2. Micas which, in addition to the above-named silicates, contain also silicates of bivalent metals (Mg, Fe, Ba, &c.). These are called, according to their composition, magnesia-, iron-, and baryta-micas.

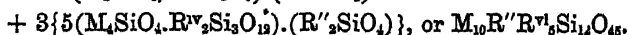
The alkali group of micas has three sub-divisions:—(A) soda-micas; (B) potash-micas; (C) lithia-micas. The analytical figures, atom-ratios, and notes of physical characteristics of members of these and of other groups are contained in the original paper. Here only the general formulæ which the author has assigned to each group will be given, M representing a univalent atom (Na, K, Li), R' a bivalent atom, and R'' the sexvalent  $\text{Al}_2$ ,  $\text{Fe}_2$ . It must be understood also that O may be replaced by  $\text{Fl}_2$ .

A. *Soda-micas* have the formula  $2(\text{H}_4\text{SiO}_4)(\text{Na}_4\text{SiO}_4)3(\text{Al}_2\text{Si}_2\text{O}_{12})$ , or  $\text{M}_2\text{AlSi}_2\text{O}_8$ .

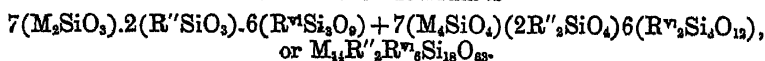
B. *Potash-micas*.—*First division*. Usually the formula is—



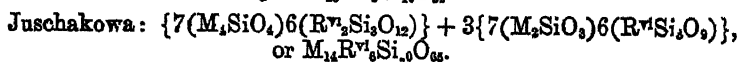
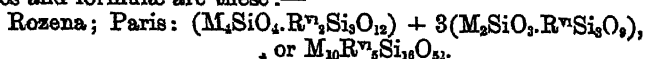
In most cases these have  $\text{H} : \text{K} = 2 : 1$ , but the proportion  $\text{M} : \text{R}' = 2 : 1$  is not invariable. To this division belong micas from Pontivy, Unionville, Litchfield, Utö, Goshen (Mass.), Lanne's Mine, Lisens (Tyrol), Bengal, Horrsjöberg, East Indies, Ballygihen, Grindelwald, Easton (Pennsylv.), Ceux, Leinster, Glendalough, &c. The *second division* of the potash-micas is sub-divided into two series, the first of which contains micas from the Zillerthal, Royalston, Aschaffenburg, Brodallo near Fahlun, Soboth, Ochozk, and Ytterby (Sweden). Their general formula is  $5(\text{M}_2\text{SiO}_4.\text{R}'\text{Si}_2\text{O}_6).(\text{R}''\text{SiO}_3)$



The second series of the second division of the potash group are less basic than the first division. Their formula is—



C. *The Lithia-micas*.—These contain no hydrogen, and appear to consist of 1 mol. of orthosilicate with 3 mols. of bisilicate. The localities and formulæ are these:—



In the second great division of the micas, the *magnesia-micas* containing nearly 30 per cent. of magnesia and little or no iron, are first considered. The specimens referred to are from Rossie, St. Lawrence, N.Y.; Gouverneur, St. Lawrence, N.Y.; Jefferson Co., N.Y.; Edwards, St. Lawrence, N.Y.; Paragas, Finland; Pennsbury, Pennsylv.: and Ratnapura, Ceylon. The author hesitates whether to regard this group as consisting of 4 or of 3 mols. of orthosilicates with 1 mol. of bisilicate. He pronounces finally, however, for the latter view, as more closely representing the analyses. The most general formula of the group is  $M_{14}R''_{25}R^v_7Si_{36}O_{126}$ .

*Iron-magnesia-nucas*, *Magnesia-iron-micas*, and *iron-micas*, form another section of the groups discussed in the present paper, which contains, however, only the first division, viz., the *iron-magnesia-micas*. The specimens mentioned belonging to this first division are from Vesuvius; Morawitz; Tschibarkul, Siberia; Monzoni; Lake Baikal, Siberia; Mainland; Arendal; and Greenwood Furnace, Monroe, N.Y. All the micas of this section consist entirely of orthosilicates. The general formulæ for the numbers of the first division (*iron-magnesia-micas*) is—



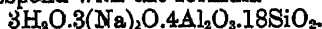
R. R.

**Composition of Cymatolite from Goshen (Mass.).** By A. A. JULIEN (*Am. J. Sci.* [3], 17, 398).—A specimen identical in physical character with that found by Shephard in the granite veins of Hampshire Co., Mass., yielded the following results:—

|                                      |       | Oxygen. |
|--------------------------------------|-------|---------|
| Water .....                          | 2.58  | 2.29    |
| Nitrogenous organic matter ....      | 0.43  | —       |
| K <sub>2</sub> O .....               | 8.38  | 1.42    |
| Na <sub>2</sub> O .....              | 2.57  | 0.66    |
| Li <sub>2</sub> O .....              | 0.09  | 0.05    |
| CaO .....                            | 0.48  | 0.14    |
| MgO .....                            | 0.75  | 0.30    |
| MnO .....                            | 0.18  | 0.04    |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 1.66  | 0.49    |
| Al <sub>2</sub> O <sub>3</sub> ..... | 24.38 | 11.38   |
| SiO <sub>2</sub> .....               | 58.11 | 30.99   |

99.61

These numbers correspond with the formula—



The author proposes to retain the name *aglaite* for this peculiarly brilliant and micaceous variety of cymatolite.

J. M. H. M.

**Associated Minerals contained in certain Trachytes from the Ravine of Riveau Grande, at Mont Dore.** By F. GOUNARD (*Compt. rend.*, 89, 614—616).—In a memoir by Koch, Professor of Mineralogy at Klausenberg, on andesite from Mount Arany, and on the minerals associated therewith, two new specimens are described, namely, *szaboite* and *pseudobrookite*. One of these, *szaboite*, having been found by the author in a specimen of trachyte accidentally

picked up in the ravine of the Riveau Grande at Mont Dore, it was thought that a more careful investigation of the rocks of that locality might lead to the discovery of a similar association of minerals as that described by Koch as emanating from Mont Arany. Without pretending to describe the situation and the exact circumstances under which they were eventually found, it will be sufficient to say that both minerals, szaboite and pseudobrookite, undoubtedly exist in the trachyte of the Riveau Grande, associated with tridymite, altered hornblende, and sometimes with breislakite. Szaboite has since been discovered by Lasaulx on the lava of Biancavilla, to the south of Etna.

J. W.

**The Lavas of the Volcanos of Ernici in the Valle del Sacco (Rome).** By S. SPECIALE (*Gazzetta*, 9, 393—395). These lavas are of a dark-grey colour, that from the volcano Giuliana having a sp. gr. 2·5, and that of Pofi 2·81 at 15°. The analyses of the two lavas gave the following results:—

|             | SiO <sub>2</sub> . | P <sub>2</sub> O <sub>5</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | FeO.                                  | CaO.  |
|-------------|--------------------|---------------------------------|----------------------------------|----------------------------------|---------------------------------------|-------|
| Giuliano .. | 46·22              | 0·52                            | 22·47                            | 8·97                             | 0·78                                  | 12·18 |
| Pofi .....  | 47·59              | 0·51                            | 18·02                            | 6·44                             | 1·19                                  | 11·66 |
|             | MgO.               | CuO.                            | K <sub>2</sub> O.                | Na <sub>2</sub> O.               | CO <sub>2</sub> and H <sub>2</sub> O. |       |
| Giuliano .. | 3·35               | 0·30                            | 5·42                             | 1·02                             | 0·56                                  |       |
| Pofi .....  | 2·41               | 0·23                            | 10·05                            | 1·82                             | 0·72                                  |       |

C. E. G.

**A Meteorite which fell on January 31, 1879, at la Bécasse; Commune of Dun-le-Poëlier (Indre).** By DAUBRÉE (*Compt. rend.*, 89, 597—598).—The fall of this meteorite was accompanied by a violent detonation, audible at a distance of 20 kilometers; its path was nearly vertical, and its velocity such that it embedded itself in the soil about 0·3 meter. It weighed 2·8 kilograms; in form it roughly resembled a pyramid with a square base, the angles being rounded off; the surface was covered with a black hard crust similar to that of other meteorites. The interior of the meteorite presented a finely-grained structure and a clear grey colour, throughout which numerous metallic grains were distributed. The matrix was chiefly peridot and a bisilicate such as pyroxene or enstatite; the metallic portion consisted of nickeliferous iron and troilite. The meteorite consequently belongs to the group of sporadosiderites, and to the subgroup of oligosiderites, numerous representatives of which are known.

J. W.

**Water of the Oberbrunnen, Flinsberg, Silesia.** By T. POŁECK (*Ber.*, 12, 1902—1906).—This spring yields about 1,000 litres per hour; the water is clear, sparkling, and colourless, has a chalybeate taste, but no odour. Its temperature is 7°, that of the air being 14·5°. It has a slightly acid reaction, but after boiling its action is alkaline.

Its analysis gave the following results.

10 litres of the water contain:—

|                                   |             |
|-----------------------------------|-------------|
| Sodium chloride .....             | 0·0618 gram |
| Potassium chloride .....          | 0·0253 "    |
| Potassium sulphate .....          | 0·1041 "    |
| Sodium carbonate.....             | 0·4705 "    |
| Lithium     " .....               | 0·0101 "    |
| Ammonium .....                    | 0·0107 "    |
| Calcium .....                     | 0·9648 "    |
| Magnesium .....                   | 0·7245 "    |
| Iron .....                        | 0·2442 "    |
| Manganese .....                   | 0·0067 "    |
| Aluminium phosphate .....         | 0·0087 "    |
| Silica .....                      | 0·3995 "    |
| Titanic acid .....                | 0·0026 "    |
| Half-combined carbonic acid ..... | 3·0356 "    |
|                                   | 0·1055 "    |

Free carbonic acid 25·429 grams corresponding to 13,229 c.c. at 7°.

The following are also present, but in quantities too small to be weighed, viz., iodine, boric and arsenic acids, antimony, tin, nickel, bismuth, barium, and strontium.

The analysis of the ochre-sediment from the spring gave the following results:—

|                                  |                 |
|----------------------------------|-----------------|
| Water (expelled at 120°) .....   | 32 15 per cent. |
| Iron oxide .....                 | 43·75 "         |
| Calcium carbonate .....          | 0·57 "          |
| Magnesium carbonate .....        | 0·30 "          |
| Barium sulphate .....            | 0·014 "         |
| Manganese .....                  | 0·027 "         |
| Copper .....                     | 0·015 "         |
| Nickel.....                      | 0·003 "         |
| Bismuth .....                    | 0·003 "         |
| Phosphoric acid.....             | 1·43 "          |
| Silica .....                     | 3·16 "          |
| Titanic acid .....               | 3·13 "          |
| Insoluble residue, sand, &c..... | 7·86 "          |
| Loss on ignition .....           | 7·35 "          |
| Aluminium.....                   | (not estimated) |

Arsenic acid, antimony, and tin, are present, but in quantities too small to be weighed.

These results are of interest, inasmuch as they show the presence in the water of this spring of constituents of the minerals which are found in the mountains in its neighbourhood, and also as one of the few instances we have of springs containing titanic acid.

P. P. B.

## Organic Chemistry.

**Halogen Derivatives of Ethane and Ethylene.** By J. DENZEL (*Ber.*, 12, 2207—2208).—*Chloropentabromethane*,  $C_2ClBr_5$ , prepared by the action of bromine on chlorotribrom- and tetrabrom-ethane, is deposited from carbon bisulphide in crystals which melt, with decomposition, at  $170^\circ$ .  *$\alpha$ -Dichlorotetrabromethane*,  $C_2Br_4Cl_2$ , obtained by the action of bromine on  *$\alpha$ -dichlorodibromethane*, forms colourless crystals, which evolve bromine at  $175^\circ$ , and melt with complete decomposition at  $180^\circ$ . *Hexabromethane*,  $C_2Br_6$ , *pentabromethane*,  $C_2HBr_5$  (colourless crystals, m. p.  $54^\circ$ , b. p.  $210^\circ$ , under 300 mm. pressure), and *tetrabromethane* (b. p.  $195^\circ$  under 300 mm., and  $225^\circ$  under 732 mm. pressure), are derived from  $\beta$ -tribromethane. Unsymmetrical tribromethane has not yet been prepared. *Chlorotribromethylene*,  $C_2ClBr_3$ , from chlorotetrabromethane, melts at  $34^\circ$ , and boils at  $203$ — $205^\circ$  under 734 mm. pressure (comp. this Journal, 1879, Abst., 368). W. C. W.

**Action of Silver Cyanate on Isobutyl Iodide.** By B. BRAUNER (*Ber.*, 12, 1874—1877).—In a former communication, the author and Linnemann (*Ber.*, 11, 1243) demonstrated that the product of the action of silver cyanate on isobutyl iodide, when treated with potash, yields both trimethylcarbinylamine and isobutylamine. When isobutyl iodide and silver cyanate react on one another in a vessel connected with a reversed condenser, a volatile liquid is first formed, which afterwards disappears, gaseous butylene and cyanic acid being given off. The products of this reaction when treated with soda give tertiary butylamine and a little isobutylamine.

When isobutyl iodide is distilled repeatedly over fresh silver cyanate, tertiary butyl cyanate,  $CMe_3.NCO$ , is obtained. It is a colourless liquid of aromatic odour, b. p.  $85.5^\circ$  (corr.), and sp. gr. 0.8676. The determination of its vapour-density gave 3.48, the calculated being 3.42. With hydrochloric acid, it yields tertiary butylamine hydrochloride, and by the action of water it is converted into the urea,  $(CMe_3.NH)_2CO$ , m. p.  $242^\circ$ , which is also formed by the action of tertiary butylamine on the cyanate, whereas by isobutylamine the cyanate is converted into a urea of the formula,



m. p.  $163^\circ$ . Tertiary butyl cyanate, when heated at  $180^\circ$ , is resolved into butylene, cyanic acid, and cyanuric acid.

In the residue from the distillation of isobutyl iodide over silver cyanate, solid isomerides of butyl cyanate and of cyanuric acid have been detected.

Silver cyanate, when gently warmed with an excess of isobutyl iodide, yields a product which is converted into isobutylamine by the action of soda. When isobutyl iodide is distilled over silver cyanate mixed with sand, the reaction is less violent, and the chief product is isobutyl cyanate.

P. P. B.

**Constitutional Changes in the Molecule of the Isobutyl Group.** By B. BRAUNER (*Ber.*, 12, 1877—1879).—The author explains the results described in the previous abstract by supposing that intramolecular change takes place at the commencement of the reaction as follows:—



(2.) Another portion decomposes thus:  $\text{C}_4\text{H}_9\text{I} + \text{AgNCO} = \text{AgI} + \text{C}_4\text{H}_8 + \text{HNCO}$ . And finally both the cyanic acid and the butyl cyanide form solid polymerides.

P. P. B.

**Octyl Derivatives.** By E. EICHLER (*Ber.*, 12, 1879—1889).—In the preparation of the following octyl derivatives the author used the alcohol prepared from the oil of *Heracleum sphondylium*.

**Mercuric dioctyl**,  $\text{Hg}(\text{C}_8\text{H}_{17})_2$ , prepared from octyl iodide by the action of sodium-amalgam, is a clear, colourless, oily liquid, of feeble odour, producing slight headache. Its sp. gr. is 1.342 at 17°. It cannot be distilled, as it decomposes at 200° into dioctyl and mercury. It is insoluble in water, but soluble in alcohol, ether, and benzene.

**Mercuric octyl iodide**,  $\text{Hg}.\text{C}_8\text{H}_{17}\text{I}$ .—Obtained as a white silvery precipitate on treating mercuric dioctyl with iodine and alcohol.

**Mercuric octylchloride**,  $\text{HgC}_8\text{H}_{17}\text{Cl}$ , formed as a white precipitate by the action of mercuric chloride on mercuric dioctyl. When this chloride is treated with moist silver oxide, mercuric octyl hydrate,  $\text{Hg}.\text{C}_8\text{H}_{17}\text{OH}$ , is formed. It crystallises in beautiful yellow leaflets, m. p. 75°, is sparingly soluble in hot water, but abundantly in alcohol. Its solutions have an alkaline reaction, expel ammonia from its salts, and produce precipitates in solutions of ferric, aluminic, zinc, and copper salts. In the last case the precipitate is grey, and on boiling is reduced to copper.

**Dioctyl**,  $(\text{C}_8\text{H}_{17})_2$ , is prepared by the action of zinc on octyl iodide at 180°. On distilling the product, a liquid is obtained which, on cooling, solidifies to a crystalline mass (m. p. 14°, b. p. 277—279°). Its sp. gr. is 0.7438° at 15°. Its properties agree generally with those attributed to it by Zincke (*Annalen*, 152. 16); it appears, however, that some other compound is present, perhaps a small quantity of dioctylene.

**Nitro-octane**,  $\text{C}_8\text{H}_{17}\text{NO}_2$ .—This body was prepared by V. Meyer's method (*Annalen*, 171, 23), viz., by the action of silver nitrite on octyl iodide; the product of this reaction is a bright yellow liquid which, when distilled, yields two fractions, the first consisting of octyl nitrite (b. p. 171—180°), the second of nitro-octane, boiling at 205—212°. The latter with nitrous acid and alcoholic potash gives the reactions shown by Meyer to be characteristic for primary nitro-compounds.

**Octylnitrolic acid** was obtained as a syrup by the action of nitrous acid on the nitrolic acid: when treated with sulphuric acid it gave octylic acid.

**Octylamine**,  $\text{C}_8\text{H}_{17}\text{NH}_2$ .—This the author prepared by reducing the nitro-octane with iron filings and acetic acid; it has already been



obtained by Van Renesse, according to whom it unites with water, forming a crystalline compound,  $C_8H_{17}N + H_2O$ . This compound, however, the author finds to be the carbonate,  $(C_8H_{17}N)_2CO_3$ , as it gives off carbonic anhydride when heated with acid.

*Octyl nitrite*,  $C_8H_{17}O.NO$ , is prepared by passing nitrous acid into octyl alcohol, and heating in closed vessels at  $100^\circ$ . It boils at  $175-177^\circ$ ; its sp. gr. is 0.862 at  $17^\circ$ . It is insoluble in water, but easily soluble in ether and alcohol.

*Octyl cyanide*,  $C_8H_{17}CN$ .—Prepared in the usual manner from octyl iodide and potassium cyanide; it is a liquid boiling at  $214-216^\circ$ ; its sp. gr. is 0.786 at  $16^\circ$ ; is insoluble in water, but easily soluble in alcohol and ether.

P. P. B.

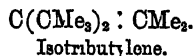
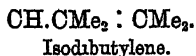
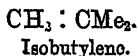
**Fluoborethylene.** By C. COUNCLER (*Ber.*, 12, 1967).—The formula,  $C_2H_5BFO_2$ , ascribed by Landolph (*Ber.*, 12, 1586) for fluoborethylene is incorrect, since it contains an odd number of perissad atoms. The formula,  $BF(OH).OC_2H_5$ , which also represents its constitution, agrees better, both with the mode of formation and with the reactions of the compound.

T. C.

**Isotributylene.** By A. BUTLEROW (*Ber.*, 12, 1482—1486).—Whilst trimethylcarbinol is formed as an intermediate product during the conversion of isobutylene into isodibutylene, *tri-isobutylene* is readily obtained at ordinary temperatures, and apparently without hydration, when isobutylene is absorbed by a moderately cool mixture of 5 parts of oil of vitriol and 1 part of water. The oily layer which separates yields pure isotributylene as a colourless mobile strongly refracting liquid, of b. p.  $177.5-179^\circ$  and sp. gr. 0.774 at  $0^\circ$ , 0.746 at  $50^\circ$ . This hydrocarbon slowly absorbs oxygen when exposed to air or when heated with it at  $190^\circ$ . Bromine combines with it energetically, but the product soon begins to evolve hydrobromic acid. It does not readily combine with haloid acids nor with sufficient hydrogen for saturation. By oxidation with chromic mixture at ordinary temperatures it yields carbonic, acetic, and trimethylacetic acids, acetone and indifferent oils, but principally a feebly acid body of the composition  $C_{11}H_{22}O_2$ . This is crystalline, insoluble in water, soluble in alcohol and ether, and distils unchanged at  $266^\circ$  (m. p.  $66-70^\circ$ ). Although it can decompose carbonates in the cold, it is precipitated from its solutions in alkalis by carbonic anhydride, and its ammoniacal solution on evaporation over oil of vitriol leaves the free acid. The sodium salt has the composition  $2(C_{11}H_{21}NaO_2) + H_2O$ . Potassium and magnesium salts are also described. The alkaline compounds are decomposed by the carbonic acid of the atmosphere. They yield white precipitates with solutions of barium, strontium, calcium, lead and silver salts. The methyl salt boils at  $217-220^\circ$ , the ethyl salt at  $227-230^\circ$ .

The indifferent oils above mentioned boil between  $100$  and  $200^\circ$ , and have all the characters of ketones.

The experiments of Fr. Lermontoff (*Ber.*, 11, 1255) tend to prove that isotributylene is a tertiary-butyl derivative of isodibutylene, probably thus constituted:—



i.e., it is unsymmetrical *dimethyl-dikatabutylethylene*, analogous to the hexylene (tetramethylethylene) corresponding with and convertible into pinacone (Paulow). Now, when pinacone is acted on by an acid, one of its methyl groups is transferred from one carbon atom to the other, producing a derivative (pinacolin) in which one carbon atom is united to *three* methyl groups. Admitting that a similar intramolecular transposition takes place during the oxidation of isotributylene, the first product from it would be the pinacolin  $\text{CH}_3.\text{CO}.\text{CMe}(\text{CMe}_3)_2$ , which would be further oxidised to *methyl-dikatabutylacetic acid*,  $\text{CMe}(\text{CMe}_3)_2.\text{COOH}$ , the crystalline acid described above. The intermediate pinacolin may be present amongst the oily neutral products of the reaction. It is also possible that part of the hydrocarbon may be oxidised without transposition, and, the splitting of the molecule taking place at the point of double union of carbon atoms, acetone and dikatabutyl-ketone would result, the first giving acetic acid, the second trimethylacetic acid, by further oxidation.

If this theory be correct, the acid  $\text{C}_{11}\text{H}_{22}\text{O}_2$  should not be produced by oxidising isotributylene in neutral or alkaline solution, and the oxidation of other tetra-substituted ethylenes in acid solution should yield acids containing an atom less of carbon. Both anticipations have been confirmed. When isotributylene is oxidised with potassium permanganate, it yields only acetic and trimethacetic acids, together with indifferent oils, whilst tetramethylethylene by oxidation with chromic mixture gives acetone, acetic acid, and some trimethacetic acid.

The conversion of isobutylene into isotributylene is probably brought about by successive hydrations and dehydrations, although these have not been demonstrated.

Ch. B.

**The Hydrocarbon,  $\text{C}_{10}\text{H}_{16}$ , from Diamylène.** By TUGOLESSOFF (*Ber.*, 12, 1486).—This hydrocarbon is not identical with terebene, as Bauer states, since it is not convertible into cymene and does not yield terephthalic acid by oxidation.

Ch. B.

**Action of Ferro- and Ferri-cyanic Acids on Amines.** By L. J. EISENBERG (*Ber.*, 12, 2234).—*Aniline ferrocyanide*,  $4(\text{C}_6\text{H}_5)\text{NH}_2.\text{H}_4\text{FeCy}_6$ , crystallises in white scales. The ferro- and ferri-cyanides of ortho- and meta-toluidine, acetamide, naphthylamine, and bromaniline were also prepared.

W. C. W.

**On the Addition of Oxygen to Unsaturated Compounds.** By L. HENRY (*Ber.*, 12, 1838–1844).—From tetrachlorethyl oxide,  $\text{CCl}_3.\text{CHCl}.\text{OEt}$  (*Ber.*, 4, 101 and 435), the compound  $\text{CCl}_2 : \text{CCl}.\text{OEt}$  (*ibid.*, 11, 445 and 750: 5, 1054) has been obtained. This and the corresponding methyl derivative,  $\text{CCl}_2 : \text{CCl}.\text{OMe}$ , on exposure to the air give off hydrochloric acid, become moist, and are finally converted into oxalic acid. Pure dry oxygen unites with the oxy-derivatives of perchlorethylene, apparently forming an acid chloride of the constitution  $\text{COCl}.\text{CCl}_2(\text{OOC}_n\text{H}_{2n+1})$ , which is therefore easily resolved into

oxalic acid. This compound is a dichloro-derivative of oxalovinyl chloride (*ibid.*, 4, 598).

The author also criticises the views of Demole (*ibid.*, 11, 315) and of Fittig (*Annalen*, 195, 176) upon the compounds formed by the addition of oxygen to the haloïd-derivatives of ethylene. The formation by these reactions of bodies exhibiting the properties of oxychlorides and bromides,  $\text{COCl}$  and  $\text{COBr}$ , and of analogous bodies by the action of heat on perchlorinated ether, the author considers to belong to the same class.

P. P. B.

**Preparation of Propylene Glycol from Glycerol.** By A. BELOHOUBEK (*Ber.*, 12, 1872—1874).—According to Letts, the gum-like mass obtained by treating glycerol with sodium amalgam is sodium glycerate. This substance, when submitted to dry distillation, yields as chief product a colourless liquid, most of which on fractionation passes over at 186—188°. The analysis and physical properties of this liquid show it to be propylene glycol; it boils at 187° (cor.), its sp. gr. is 1.054 (Wurtz, 1.051), and the vapour-density 2.68. When it is heated with hydrochloric acid the corresponding chlorohydrin is formed, which yields propylene oxide, b. p. 36°, by treatment with potash.

This formation of propylene glycol from glycerol the author regards as uninfluenced by nascent hydrogen, laying particular stress on the formation of water. When glycerol is distilled with soda, propylene glycol is also formed, together with some acids and hydrocarbons.

P. P. B.

**Some Properties of Glucose.** By PÉLIGOT (*Compt. rend.*, 89, 918—922).—Saccharose, when treated with lime, gives a compound, but glucose yields glucate of calcium and tribasic glucate of calcium, coloured brown by melassic acid, a humus-like body. The author has succeeded in isolating a substance of the formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , an isomeric of saccharose, by the following process:—After boiling a solution of glucose and lime, and filtering to separate a brown precipitate, enough oxalic acid is added to throw down all the lime. After allowing the filtrate to stand for a long time, crystals separate and the adhering syrup is removed by means of blotting-paper. The crystals are dissolved in hot water, and the solution is decolorised by animal charcoal. On spontaneous evaporation, the new substance, to which the author has given the name *saccharin*, separates in bulky prisms. It may also be purified by dialysis. Another method is to add subacetate of lead to a neutral solution of calcium glucate and *saccharin*; tribasic glucate of lead separates out, and the filtrate on addition of ammonia gives a deposit of a compound of *saccharin* and lead oxide, from which the former may be isolated by sulphuretted hydrogen or by sulphuric acid.

*Saccharin* is not a sugar; it does not ferment; it has not a sweet taste, but a slightly bitter after-taste, recalling Glauber's salt. It is sparingly soluble in cold water, but easily in hot water. It is partly volatile without decomposition; it is almost unattacked by nitric acid, and is dissolved by sulphuric acid without alteration. It reduces Fehling's solution, but not until after prolonged ebullition. The author remarks in conclusion, that *saccharin* and glucic acid differ

from glucose only by elimination of water, and imagines the action of lime on glucose to be analogous to saponification. W. R.

**Remarks on the Saccharoses.** By BERTHELOT (*Compt. rend.*, 89, 965—966).—The author draws attention to the close resemblance in crystalline form of the *saccharine* recently discovered by Peligot, and trehalose, the crystalline form and angles being nearly identical, although the stability is different, and the formula of trehalose shows it to be hydrated. He also offers some remarks on the relative stability of the saccharoses under the action of dilute sulphuric acid.

W. R.

**On Tunicin.** By FRANCHIMONT (*Compt. rend.*, 89, 755—756).—By the action of sulphuric acid on tunicin or animal cellulose, Berthelot, and lately Schäfer, have obtained a sugar which the author on examination finds to be dextrose. The difference between animal and vegetable cellulose is to be attributed to a difference in the manner in which the groups  $C_6H_{10}O_5$  are connected, and not to a difference in the individual groups. L. T. O'S.

**Calcination of Beetroot Molasses.** By C. VINCENT (*Compt. rend.*, 89, 788—790).—The author replies to Duvillier and Buisine's remarks (*ibid.*, 89, 48; this Journal, 36, 912), and confirms his previous statement that the basic products consist chiefly of ammonia and trimethylamine, the amount of dimethylamine being but small.

L. T. O'S.

**Action of Cyanamide on Dimethylamine Hydrochloride.** By P. TATARINOFF (*Compt. rend.*, 89, 608).—As methylguanidine is formed by the action of cyanamide on methylamine hydrochloride, so dimethylguanidine is formed by the action of the same substance on dimethylamine hydrochloride. An alcoholic solution of the two substances is heated for several hours at 105—110°, the excess of dimethylamine is removed, and the dimethylguanidine separates in the form of the platinochloride. Its analysis calculated accurately to the formula  $(C_2H_5N_3.HCl)_2PtCl_4$ .

J. W.

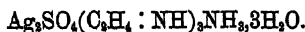
**Chloro-derivatives of Amines.** By H. KÖHLER (*Ber.*, 12, 1869—1872).—Wurtz (*Compt. rend.*, 11, 810) and Wilm (*Ber.*, 8, 427) state that dichlorethylamine undergoes decomposition when kept; whilst Tscherniak (*Ber.*, 9, 143) attributes this decomposition to impurities. The author has prepared dichlorethylamine according to the method proposed by the latter, and obtained it pure. After this preparation had stood some months in a stoppered bottle, the liquid had become solid, and amongst the products of decomposition the following were observed:—Hydrochloric acid, ammonium chloride, monethylamine hydrochloride, chloroform, acetonitril and acetic chloride. The formation of some of these compounds may be explained as follows:—

- (1.)  $CH_3.CH_2.NCl_2 + H_2O = CH_3.COCl + HCl$
- (2.)  $CH_3.CH_2.NCl_2 = CH_3.CN + 2HCl$
- (3.)  $CH_3.CH_2.NCl_2 + 2HCl = CH_3.CH_2.NH_2 + 2Cl_2$
- (4.)  $CH_3.CH_2.NCl_2 + 3Cl_2 = CCl_3.CH_2.NH_2 + 3HCl$
- (5.)  $CCl_3.CH_2.NCl_2 = CHCl_3 + CNCl + HCl$

P. P. B.

**Ethylidenamine Silver Sulphate.** By W. G. MIXTER (*Am. J. Sci.* [3], 17, 427—429).—In order to prepare this compound, aldehyde-ammonia is dissolved in a small quantity of water, and silver sulphate, in the proportion of 1 molecule to 4 molecules of aldehyde-ammonia, is slowly added with constant agitation; after some hours, the small black residue is filtered off, and the filtrate is left to spontaneous evaporation, when colourless transparent crystals separate, which give the aldehyde reaction strongly. At summer temperatures, tabular crystals, and at 10—15°, prismatic crystals, predominate.

The tabular crystals, dried between blotting-paper, and then washed with alcohol and ether successively, gave on analysis results from which the author deduces the formula  $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4:\text{NH})_4 \cdot 3\text{H}_2\text{O}$ , whilst the elongated crystals gave results agreeing with the formula  $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4:\text{NH})_4 \cdot 6\text{H}_2\text{O}$ . Some crystals apparently of the same form as the tabular crystals, gave the formula,



*Ethylidenamine silver sulphate* is soluble in water, and yields aldehyde when treated with acids. The hexhydrated salt loses water more readily in dry air than the trihydrated. J. M. H. M.

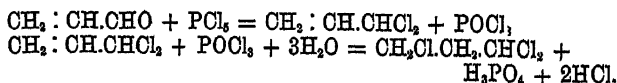
**Bases from Fusel Oil.** By H. SCHRÖTTER (*Ber.*, 12, 1431—1432).—By agitating with hydrochloric acid that part of fusel oil (from beetroot molasses) which boils above 200°, the author has extracted a mixture of basic bodies boiling between 180 and 230°. This appears to include at least two bases having the composition  $\text{C}_6\text{H}_{12}\text{N}_2$  and  $\text{C}_{10}\text{H}_{18}\text{N}_2$ , respectively. The first of these forms a crystalline sulphate,  $\text{C}_6\text{H}_{12}\text{N}_2(\text{H}_2\text{SO}_4)_2$ . Their examination is not yet completed.

Ch. B.

**Hydrazines of the Fatty Series.** By E. FISCHER (*Annalen*, 199, 281—325).—The substance of this paper has appeared in the *Berichte* from time to time and has been abstracted in this Journal.

**$\beta$ -Chloropropaldehyde.** By KRESTOWNIKOFF (*Ber.*, 12, 1487—1488).—This aldehyde, formed by the union of hydrochloric acid with acrolein (*Ber.*, 10, 1104), crystallises from alcohol in long thin colourless needles (m. p. 34·5—35·5°), which decompose on keeping; it is sparingly soluble in water, easily in alcohol and ether, and gives  $\beta$ -chloropropionic acid when oxidised with nitric acid of 1·4 sp. gr.

By acting on acrolein with phosphoric chloride, Genthner believed that he had formed acrolein chloride, and a compound of dichloroglycide and trichlorhydrin isomeric with it. The author, however, suspects that this so-called compound was in reality *isotrichlorhydrin*, produced by the successive reactions—



He notes that the boiling point of this compound (144—148°) is lower than that of trichlorhydrin, agreeing with the law that the boiling points of all halogen derivatives of hydrocarbons, in which the

halogen atoms are united to one carbon atom, are lower than those of their isomerides.

Dichloroglycide, he considers, is formed by separation of HCl from this isotrichlorhydrin—



a decomposition which may be assumed to take place in presence of certain bodies, although isotrichlorhydrin, when pure, may be distilled unchanged. Geuther and Reboul state that trichlorhydrin may be formed by addition of HCl to the isomeric dichloroglycides  $\text{CH}_2\text{Cl}.\text{CH} : \text{CHCl}$  (b. p.  $109^\circ$ ) and  $\text{CH}_2 : \text{CCl}.\text{CH}_2\text{Cl}$  (b. p.  $94^\circ$ ); but this is not in harmony with the law which regulates such syntheses, and requires confirmation. The author thinks that these chemists really had to do with two isomerides of trichlorhydrin,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{CHCl}_2$  and  $\text{CH}_3.\text{CCl}_2.\text{CH}_2\text{Cl}$ .  
Ch. B.

**$\beta$ -Chlorobutyraldehyde.** By KARETNIKOFF (*Ber.*, 12, 1488—1489).—This body is formed by the union of hydrochloric acid and crotonaldehyde.



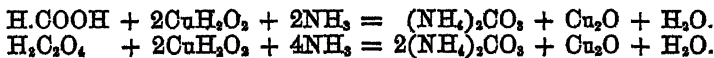
and yields  $\beta$ -chlorobutyric acid by oxidation with nitric acid (1.4 sp. gr.).

From this the author infers that when addition of HCl to a molecule takes place, the chlorine unites with the atom of carbon most remote from the oxygenised group; whilst the reverse occurs when a halogen is introduced by substitution. This generalisation is contradicted by Hemilian's observation that  $\alpha$ -derivatives are chiefly produced by the union of HBr and HI with solid crotonic acid; whilst Linnemann obtained  $\beta$ -compounds alone by the action of haloïd acids on acrylic acid. The author refers these different results to differences of temperature.  
Ch. B.

**Some Reactions of Acroleïn and Glycerol.** By TAWILDAROFF (*Ber.*, 12, 1487).—The author cannot confirm Alsberg's statement, that triethylglycerol is produced by heating acroleïn with absolute alcohol and acetic acid. When acted on by lime, glycerol yields acetone, a compound of the formula  $\text{C}_6\text{H}_{12}\text{O}$ , boiling at  $160^\circ$ , and gases containing carbon, which are not absorbed by bromine. The author is studying the action of zinc chloride on glycerol.  
Ch. B.

**Oxidation of Formic Acid and Oxalic Acid by Ammoniacal Cupric Oxide.** By P. CAZENNEUVE (*Bull. Soc. Chim.* [2], 32, 277—278).—The author gives the first results of a research into the oxidation of the acids of the acetic series by ammoniacal cupric oxide, a reagent which has already been employed by Loew for the oxidation of uric acid, creatinine, &c.

Both formic and oxalic acids, when heated for five hours at  $150^\circ$  in sealed tubes with excess of ammoniacal cupric oxide, are completely transformed into carbonic acid, the following equations being realised:—



If cupric oxide is not present in excess, part of the copper is obtained in the metallic state.

J. M. H. M.

**Dry Distillation of Sodium Trichloracetate.** By L. HENRY (*Ber.*, 12, 1844—1848).—According to the observations of Kolbe (*Annalen*, 49, 341), the salts of trichloroacetic acid are resolved by distillation into chloride of the metal, carbonic oxide, and carbonic chloride. Besides these substances, the author has observed the formation of carbonic anhydride, trichloroacetyl chloride,  $\text{CCl}_3\text{COCl}$ , and, as secondary products, trichloroacetic acid and its anhydride. Carbon tetra- and hexa-chloride have also been isolated.

P. P. B.

**Action of Aluminium Chloride on Acetic Chloride.** By W. WINOGRADOFF (*Ber.*, 12, 1486—1487).—One mol. aluminium chloride and 4 mols. of acetic chloride react when gently heated together, giving off 4 mols. of hydrochloric acid and forming a solid mass. The latter evolves 1 mol. of carbonic anhydride on treatment with water, and the distillate from the aqueous solution contains an oil lighter than water, which smells like acetone, and forms a crystalline compound with potassium bisulphide (bisulphite?). The investigation is being continued.

Ch. B.

**Characteristic Reaction of Thioglycollic Acid.** By R. ANDREASCH (*Ber.*, 12, 1390—1392).—If a drop of dilute ferric chloride solution is added to a slightly acidified solution of a thioglycollate, a transient indigo-blue colour appears, and on adding ammonia in excess, the solution takes a deep violet-red colour, which becomes more intense on agitating it with air, oxygen being absorbed. The colour disappears on standing, but may be reproduced by shaking with air.

If much ferric chloride is added in the first instance, and then ammonia in excess, the red colour at once appears. As before, it gradually fades, but may be recalled by agitating it with air. These colour-changes may be alternately produced many times, but they finally cease when the acid is completely destroyed, and all iron is then precipitated as sesquioxide.

In this reaction, *ammonium ferrid-thioglycollate*,

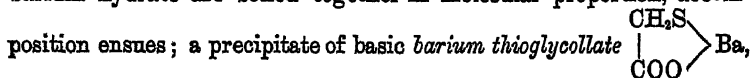


is probably first formed. On standing, this is reduced to a colourless ferrous compound, part of the acid being at the same time oxidised. Contact with air reproduces the ferric compound, which again decomposes, these changes continuing until all the acid has been oxidised. Claesson (*Annalen*, 187, 120) has observed that the cupric salt of thioglycollic acid gradually decomposes into a cuprous salt.

These reactions are not exhibited by the *thiodiglycollic acid* of Schultze and Wislicenus (*Annalen*, 146, 156).

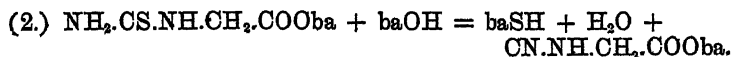
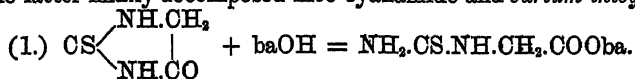
Ch. B.

**Decomposition of Thiohydantoin by Barium Hydrate.** By R. ANDREASCH (*Ber.*, 12, 1385—1390).—When thiohydantoin and barium hydrate are boiled together in molecular proportion, decomposition ensues; a precipitate of basic *barium thioglycollate*



falls, and the filtrate, when freed from barium by carbonic anhydride and evaporated, leaves an orange residuc, from which *dicyanamide* may be extracted. The precipitate, when suspended in water and treated with carbonic anhydride, is converted into the soluble normal *barium thioglycollate*  $(\text{HS} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Ba}$ ; and a solution of the latter, treated with mercuric chloride as long as the precipitate formed is re-dissolved, yields the characteristic mercury salt,  $\text{Hg}(\text{S} \cdot \text{CH}_2 \cdot \text{COOH})_2$ , described by Claesson. Thioglycollic acid was discovered by Carius (*Annalen*, 124, 43), and further studied by Heintz (*ibid.*, 136, 223), Wislicenus (*ibid.*, 146, 145), Claesson (*ibid.*, 187, 113), and others.

The author considers that dicyanamide is not directly formed from thiohydantoin, but is produced by the action of the alkali on *cyanamide*. He represents the reaction as occurring in three stages, in the first of which *barium thiohydantomate* is formed. This is subsequently converted into *barium cyanidoacetate* by removal of  $\text{H}_2\text{S}$ ; and the latter finally decomposed into cyanamide and *barium thioglycollate*.



This experiment explains why all attempts have failed to convert thiohydantoin into glycolyl-cyanamide by the action of alkalis.

Ch. B.

**Spontaneous Oxidation of Nitrolactic Acid.** By L. HENRY (*Ber.*, 12, 1837—1838).—Nitrolactic acid on keeping is resolved into oxalic and hydrocyanic acids and water, thus:  $\text{CH}_3 \cdot \text{CH}(\text{NO}_2) \cdot \text{COOH} = \text{C}_2\text{O}_4\text{H}_2 + \text{HCN} + \text{H}_2\text{O}$ . Light appears to influence this decomposition.

P. P. B.

**Reduction of Carbon Dioxide by Phosphorus at the Ordinary Temperature.** By A. R. LEEDS (*Ber.*, 12, 1834—1836).—The author has observed the formation of carbon oxide and small quantities of phosphoretted hydrogen when phosphorus partially covered with water stands for some time in an atmosphere of carbonic anhydride. He expresses the change by the equation,  $6\text{P} + 5\text{CO}_2 + 3\text{H}_2\text{O} = \text{P}_4\text{O}_6 + \text{P}_2\text{O}_3 + 2\text{PH}_3 + 5\text{CO}$ .

P. P. B.

**Oxidation of Carbon Oxide by Moist Air in Presence of Phosphorus at the Ordinary Temperature.** By A. R. LEEDS (*Ber.*, 12, 1836).—The author finds that carbon dioxide is formed when carbon oxide and air are allowed to stand in contact with moist phosphorus for some time.

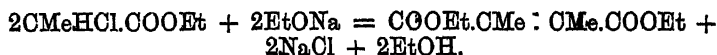
P. P. B.

**Decomposition of Mesoxalic Acid by Sulphuretted Hydrogen.** By C. BOTTINGER (*Ber.*, 12, 1956—1958).—Thioglycollic and thiodiglycollic acids are obtained, together with a little oxalic acid, when sulphuretted hydrogen is passed for many hours through a dilute aqueous solution of mesoxalic acid previously treated with silver oxide.

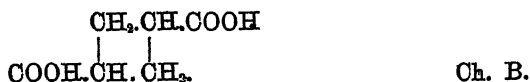
T. C.



**Homotaconic Acid.** By MARKOWNIKOFF and KRESTOWNIKOFF (*Ber.*, 12, 1489).—By adding sodium ethylate or methylate, dried at 200°, to warm ethyl  $\alpha$ -chloropropionate, the authors obtained alcohol, ethylic ethyllactate, and an ethereal salt which by saponification yielded a crystalline dibasic acid,  $C_6H_8O_4$  (m. p. 170—171°). The ethereal salt is thus produced:—



The acid is therefore unsaturated, and related to adipic acid as itaconic is to pyrotartaric acid. Hitherto the authors have not succeeded in combining it either with halogens or with haloid acids. The acid may therefore contain a closed chain—



**New Method of Preparing Thiodilactic Acid.** By C. BORTINGER (*Ber.*, 12, 1425—1426).—In his former papers (*Annalen*, 188 and 196) the author described the preparation of thiodilactic acid from pyrroacemic acid (by the action of silver oxide and hydrogen sulphide), and from  $\alpha$ -chloropropionic acid. He finds that it may also be obtained by treating pyrroacemic acid in strongly alkaline solution with hydrogen sulphide for a long time. On acidifying, shaking with ether, dissolving the ethereal extract in water, and evaporating, the acid is obtained as an uncrystallisable bright-yellow syrup. Its identity was established by the analysis of its barium salt, and by converting it into thielactic acid. Ch. B.

**Influence of Nitro- and Amido- Groups on a Sulphonic Group entering the Benzene Molecule.** By J. POST (*Ber.*, 12, 1460—1462).—It has already been observed by the author that the same bodies are produced by sulphating ortho- and para-amidophenol (*Ber.*, 6, 397), and orthobromamidobenzene (*ibid.*, 8, 1557), as by sulphating and subsequently reducing the corresponding nitro-derivatives. In each of these cases, the molecule contained a *negative* group (OH or Br) besides the nitrogen group; but in experiments which the author has since made with nitro-amido- and diamido-benzenes (meta- and ortho-), in which the second radicle is *positive*, similar results were obtained, the same *diamidobenzene-sulphonic acid* being produced from corresponding nitro- and amido-compounds. These experiments, as well as others with corresponding phenols, are as yet incomplete.

Hübner explains these phenomena by supposing that when an amido-compound is sulphated, the  $NH_2$  group, by its union with sulphuric acid, acquires negative properties, and henceforth acts like a nitro-group. To test this theory the author has repeated the experiments of Meyer and Stüber (*Annalen*, 165, 165) and of Limpriecht (*ibid.*, 177, 794). According to these, on sulphating either nitrobenzene or aniline, the *three* possible isomeric acids are produced, but one of them always predominates. By reducing the monosulphonic acid

most abundantly formed from nitrobenzene, an acid is obtained different from sulphanilic acid, the principal product from aniline. Sulphanilic acid, on the other hand, corresponds to Limpricht's *β*-nitrobenzenesulphonic acid, produced in relatively small quantity from nitrobenzene. The author completely confirms these results. He finds that nitrobenzene yields 78.6 per cent. of *α*-nitrobenzenesulphonic acid, whilst aniline yields 55.2 per cent. of sulphanilic acid. The acids were prepared and purified by well-known methods.

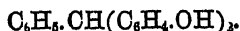
Hübner's theory, although not contradicted by these results, is not confirmed by them. Ch. B.

**Compounds of Benzotrichloride with Phenol and Tertiary Aromatic Bases.** By O. DOEBNER (*Ber.*, 12, 1462—1468).—In his first communication on this subject (*Ber.*, 11, 1236), the author described the remarkable colouring matters produced by the action of benzotrichloride,  $C_6H_5.CCl_3$ , on phenols and tertiary aromatic bases, and concluded that they are all of the same type, i.e., derivatives of triphenylmethane or of its homologues. Malachite-green,  $C_{22}H_{24}N_2$ , for example (the basic colouring matters are all green) is formed by the union of 1 mol. of benzotrichloride and 2 mols. of dimethylaniline with elimination of 3 mols. of HCl. Here the author seeks to ascertain the constitution of the red colouring matter from phenols, *benzaurin*.

When 1 mol. of benzotrichloride and 2 mols. of phenol are gently heated in an open dish, streams of hydrochloric acid are evolved. The reaction being completed on the water-bath, the red mass is freed from phenol by steam, and heated repeatedly with hydrogen-sodium sulphite solution, which dissolves out the red colouring matter, leaving a pale tenacious resin. By boiling the solution with hydrochloric acid, the colouring matter is precipitated in hard, metallic, red crusts. It is slightly soluble in water, easily in alcohol, ether, and glacial acetic acid, less easily in benzene. It forms violet-red solutions in alkalis, which become colourless on exposure to air. The colour of these alkaline solutions cannot be fixed, but the free compound dyes a golden-yellow. It melts a little above  $100^\circ$ , and decomposes at a higher temperature.

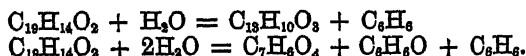
Since the colouring matter could not be obtained in a crystalline form, it was reduced in alcoholic solution with zinc and hydrochloric acid. A crystalline leuco-compound, insoluble in water, but crystallisable from alcohol, was thus obtained. It forms brilliant pale-yellow needles, which dissolve without colour in alkalis and are reprecipitated by acids. It is easily soluble in alcohol, ether, and acetic acid. It has the composition  $C_{18}H_{16}O_2$ , and is therefore formed from the colouring matter  $C_{18}H_{14}O_2$  by fixation of two atoms of hydrogen. Heated above its melting point in contact with air, it becomes red-coloured, and then yields fuchsin-coloured solutions with alkalis. Potassium dichromate and acetic acid partially oxidise it to the original colouring matter; but potassium ferricyanide converts it into a body like cedrine, insoluble in alkalis. The relation between the colouring matter and its leuco-compound is the same as that between malachite-green and its leuco-compound, or between rosolic and leucorosolic acids. Although the

number of OH groups in the molecule of the leuco-compound has not been determined, the latter doubtless has the constitution—

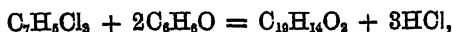


It will probably be formed by the action of benzal-chloride or benzaldehyde on phenol.

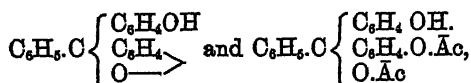
The colouring matter combines directly with acetic anhydride on heating, producing a colourless body,  $\text{C}_{18}\text{H}_{14}\text{O}_2 + \text{Ac}_2\text{O}$  (m. p.  $119^\circ$ ), which is slightly decomposed by boiling with water, slowly by alkalis, but rapidly by strong oil of vitriol. Fusing potash decomposes it, with evolution of benzene. On dissolving the fused mass in water, and acidifying, crystals of Staedel's *dihydroxybenzophenone*,  $\text{CO}(\text{C}_6\text{H}_4.\text{OH})_2$  (*Annalen*, 194, 335), are obtained. This body has also been obtained by the decomposition of *aurin* (*Ber.*, 11, 1348), and of *phenolphthalein* (*Ind.*, 11, 1299). From the filtrate *parahydroxybenzoic acid* and phenol may be extracted. The decompositions are represented by the equations:—



Reviewing these facts, the author concludes that the colouring matter is produced according to the equation—



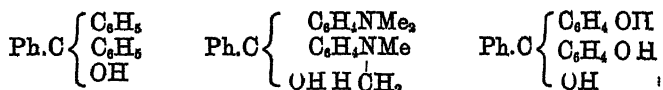
and that it and its acetyl compound have the constitutions—



also assigned to them by Graebe and Caro (*Ber.*, 11, 1351). Triphenylmethane and the leuco-compounds of malachite-green and of the phenol colouring matter are thus related:—



The colouring matters are anhydrides of similar derivatives of triphenyl carbinol—



Benzo-trichloride seems also capable of reacting with only two molecules of benzene in presence of metallic chlorides, producing only triphenylmethane in small quantity, but no tetraphenylmethane.

Ch. B.

**Separation of Orthoxylene from its Isomerides.** By WROBLEWSKY (*Ber.*, 12, 1487).—This is effected by means of its acetyl-derivative. No details are given of the method. Ch. B.

**Aniline Dithionate.** By MALTSCHESKY (*Ber.*, 12, 1487).—This salt is formed by mixing aqueous solutions of aniline sulphate and

barium dithionate. It may be precipitated by ether from an alcoholic (98 per cent.) solution in almost colourless needles, which resinify and become brown on exposure to air, giving off sulphurous anhydride. It is soluble in water and alcohol, but not in ether. At 74° it decomposes, without melting, into aniline sulphate and sulphurous anhydride.

Ch. B.

. **Amines Corresponding with  $\alpha$ -Toluic Alcohol.** By P. SPICA (*Gazzetta*, 9, 555—569).—Benzyl chloride, prepared from toluene and boiling at 227—230°, when dissolved in alcohol and treated with zinc and hydrochloric acid at a gentle heat is very slowly reduced, ten days being required for the completion of the reaction when 10 grams of the cyanide is employed. After removal of the alcohol by evaporation, the product is mixed with excess of soda, and the bases thus set free are extracted with ether in the usual way. On agitating the ethereal solution with dilute hydrochloric acid, white micaceous plates make their appearance in the ether; these are identical in every respect with the *diphenylethylamine hydrochloride*—

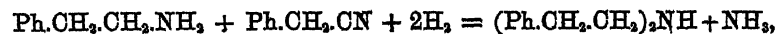


described by Fileti and Piccini (this Journal, 36, 922, and *Gaz.*, 9, 294), the crystals melt at 260° if the temperature be slowly raised, but at 265° if heated quickly. The *platinochloride* forms yellow crystals, moderately soluble in water. The dilute acid separated from the supernatant layer of ether, and evaporated to dryness, leaves a crystalline residue, a portion of which is soluble in absolute alcohol, and a portion insoluble, the latter being ammonium chloride. By evaporating the alcoholic solution, treating the hydrochlorides with soda and ether, and the ethereal solution with hydrochloric acid, a further portion of the diphenylethylamine hydrochloride may be separated, and by a long series of fractionations on the residues, small quantities of two other hydrochlorides may be isolated, the one melting at 217°, and identical with Fileti's *monophenylethylamine hydrochloride*—



(this Journal, 36, 719, and *Gaz.*, 8, 446), whilst the other (m.p. 137—138°) is *triphenylethylamine hydrochloride*  $(\text{Ph}.\text{CH}_2\text{CH}_2)_3\text{N}.\text{HCl}$ . It crystallises in long slender iridescent needles, sparingly soluble in water, easily in alcohol or chloroform, moderately in benzene, and but very slightly in ether. By spontaneous evaporation of its solution in dilute alcohol, it is sometimes obtained in long, hard, transparent prisms, which probably contain water of crystallisation, as they effloresce in a vacuum.

From these results, it is evident that the reaction is not merely the simple one expressed by the equation  $\text{Ph}.\text{CH}_2.\text{CH} + 2\text{N}_2 = \text{Ph}.\text{CH}_2.\text{CH}_2.\text{NH}_2$ , but that the phenylethylamine as soon as it is formed takes part in the reaction, thus—



and that the diphenylethylamine then yields triphenylamine by a similar reaction.

When the oily product, obtained on passing hydrogen sulphide for some time through an alcoholic solution of benzyl chloride and adding water, is reduced with zinc and sulphuric acid and treated exactly in the manner previously described for benzyl cyanide, the hydrochlorides of mono- and diphenylethylamine are formed besides some ammonium hydrochloride, but no triphenylethylamine salt. The fact that the tertiary amine is not formed in this reaction may be explained by a consideration of the different manner in which the nitrogen and carbon in the thioamide (produced by the action of the hydrogen sulphide on the nitrile), and in the nitrile are united thus:  $-\text{C} \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{NH}_2 \end{smallmatrix}$  and  $-\text{C}:\text{N}$ . With the thioamide the action of the nascent hydrogen tends to produce the monamine  $\text{Ph}.\text{CH}_2.\text{C} \begin{smallmatrix} \text{H}_2 \\ \diagup \diagdown \\ \text{NH}_2 \end{smallmatrix}$ , by displacement of the sulphur by hydrogen, and it is not improbable that the presence of the small quantity of diphenylethylamine observed is due to unaltered benzyl cyanide in the crude thioamide.

*Monophenylethylamine*,  $\text{Ph}.\text{CH}_2.\text{CH}_2.\text{NH}_2$ , obtained by the decomposition of the hydrochloride with potash and extraction with ether, is a colourless liquid somewhat lighter than water, and boiling at  $193^\circ$  under a pressure of 757.8 mm. (corr. to  $0^\circ$ ). It is easily soluble in alcohol or ether, and sparingly in water, to which it communicates a strongly alkaline reaction. The free base rapidly absorbs carbonic anhydride from the air, and becomes converted into a crystalline mass of the carbonate. Bernthsen (*Annalen*, 184, 307) states that the base crystallises in small plates, but it is not improbable that it was really the carbonate which he was examining.

*Diphenylethylamine*,  $(\text{Ph}.\text{CH}_2.\text{CH}_2)_2\text{NH}$ , is a colourless liquid (b.p.  $335-337^\circ$  at 608 mm.), somewhat heavier than water. It is soluble in alcohol and in ether, but only very sparingly in water. It combines readily with acids, but does not appear to absorb carbonic anhydride from the air.

*Triphenylethylamine*,  $(\text{Ph}.\text{CH}_2.\text{CH}_2)_3\text{N}$ , is an oily body, soluble in ether, alcohol, and chloroform, but almost insoluble in water. The quantity obtained was too small to determine its boiling point.

*Monophenylethylcarbamide*,  $\text{NH}_2.\text{CO}.\text{NH}(\text{CH}_2.\text{CH}_2.\text{Ph})$ , prepared by mixing hot solutions of potassium cyanate and monophenylethylamine hydrochloride and boiling for a few minutes, crystallises from its alcoholic solution in long flat prisms (m.p.  $112^\circ$ ). It is very soluble in alcohol and in hot water, moderately so in cold water.

*$\beta$ -Diphenylethylcarbamide*,  $\text{NH}_2.\text{CO}.\text{N}(\text{CH}_2.\text{CH}_2.\text{Ph})_2$ , obtained from diphenylethylamine hydrochloride in a similar manner to the corresponding monophenyl compounds, crystallises from boiling water in tufts of long slender prisms (m.p.  $108-109^\circ$ ). It is easily soluble in alcohol and in hot water, sparingly soluble in cold water.

The corresponding thiocarbamides were also prepared, but the quantities of material at the author's disposal were too small to enable him to examine them carefully. C. E. G.

**Ethyl Derivatives of Phenylhydrazine.** By E. FISCHER and W. EHRHARD (*Annalen*, 199, 325-332).—The mixture of volatile

bases which are produced, together with diethylphenylazonium bromide,  $\text{Ph.N}_2\text{H}_2\text{Et}_2\text{Br}$ , by the action of ethyl bromide on phenylhydrazine contains symmetrical and unsymmetrical ethylphenylhydrazine, and a series of more highly ethylated derivatives.

In order to isolate the symmetrical ethylphenylhydrazine or hydrazo-phenylethyl, the following process was adopted:—Ethyl bromide and phenylhydrazine are heated together in a flask provided with an upright condenser until the mixture solidifies; the product is dissolved in water, and the excess of ethyl bromide distilled off. A small quantity of soda is added and the solution extracted with ether. On the addition of a concentrated solution of soda to the alkaline liquid, diethylphenylazonium bromide is deposited as a white crystalline mass. The ethereal extract is evaporated to dryness, and the unaltered phenylhydrazine removed from the residue by treatment with strong hydrochloric acid. After the addition of soda to the filtrate, it is shaken up with ether and an excess of yellow mercuric oxide is added to the ethereal solution. This reagent converts the unsymmetrical ethylphenylhydrazine into a non-volatile tetrazone, and the symmetrical into a volatile azo-compound,  $\text{PhN:NEt}$ . After treatment with dilute (6 per cent.) hydrochloric acid, the ethereal liquid is evaporated, when diethylphenyltetrazone,  $\text{PhEtN.N:N.NEtPh}$ , is deposited in white monoclinic prisms, m.p.  $108^\circ$ . The mother-liquor is warmed with dilute sulphuric acid (to decompose any tetrazone contained in it), diluted with water, and extracted with ether.

By distilling in a current of steam the residue which is left on evaporating the ether, *azophenylethyl*,  $\text{PhN}_2\text{Et}$ , is obtained. The first portion of the distillate is pure, the later portion must be purified by treatment with dilute acids. The azo-compound is a pale yellow oil lighter than water. It boils between  $175$  and  $185^\circ$  with partial decomposition, and decomposes slowly on exposure to the air. It is freely soluble in alcohol, ether, and benzene, and in concentrated acids, and is rapidly attacked by reducing agents. By the action of sodium amalgam on the alcoholic solution, it yields *hydrazophenylethyl*,  $\text{Ph.NH.NH.Et}$ , which may be extracted with ether after diluting the mixture with water. The crude product is purified by precipitation as the acid oxalate,  $\text{C}_8\text{H}_{12}\text{N}_2\cdot\text{C}_2\text{H}_4\text{O}_4$ .

By decomposing the oxalate with an alkali, the free base is obtained as a colourless oil, soluble in alcohol, ether, and benzene. It distils without decomposition. Fehling's solution, mercuric oxide, nitrous acid, and even exposure to the atmosphere convert it into the azo-compound. It is decomposed by the action of zinc and acetic acid, forming ethylamine and aniline.

*Oxidation of Phenylhydrazine by Mercuric Oxide.*—In the decomposition of phenylhydrazine by Fehling's solution, nitrogen, benzene, and aniline are formed (*Ann.*, 190, 101); if mercuric oxide is substituted as the oxidising agent considerable quantities of mercury diphenyl are produced in addition to the above products of decomposition. Four grams of mercury diphenyl were obtained from 10 grams of the base.

W. C. W.

**Synthesis of Substituted Guanidines.** By E. ERLENMEYER (*Ber.*, 12, 1984—1985).—A claim of priority.

**Orthotoluidine-Guanidines and their Cyanogen-Derivatives.**

By F. BERGER (*Ber.*, 12, 1854—1860).—*Di-orthotolylthiocarbamide*,  $\text{CS}(\text{NH} \cdot \text{C}_6\text{H}_7)_2$ , was prepared by acting with carbon bisulphide on an alcoholic solution of orthotoluidine in presence of an alkali. It is insoluble in ether and water, but dissolves freely in hot benzene, acetic acid, and alcohol, from which it crystallises in long needles. The author finds its melting point to be  $158^\circ$  (uncor.), and not  $165^\circ$  as stated by Girard (*Ber.*, 5, 985).

*Diorthotolylguanidine*,  $\text{NH} : \text{C}(\text{NH} \cdot \text{C}_6\text{H}_7)_2$ , is obtained by the action of lead acetate on an alkaline solution of the above carbamide, ammonia gas being at the same time passed into the solution. On adding alkalis to the hydrochloric acid solution, a white curdy precipitate is thrown down, which, after crystallisation from alcohol, melts at  $179^\circ$ . It forms well crystallised salts, and a platinumchloride,  $(\text{C}_{12}\text{H}_{17}\text{N}_3 \cdot \text{HCl})\text{PtCl}_4$ , which is of a bright yellow powder, insoluble in the ordinary solvents.

*Dicyanodiorthotolylguanidine*,  $\text{NH} : \text{C}(\text{NHC}_6\text{H}_7)_2 + 2\text{CN}$ , is obtained by passing cyanogen into the ethereal solution of the above guanidine; it separates out in small, needle-shaped crystals; easily soluble in alcohol and benzene: when heated, it becomes brown at  $160^\circ$ , and melts at  $173.5$ — $174.5^\circ$  to a dark brown resinous mass.

*Diorthotolylloxalylguanidine*,  $\text{NH} : \text{C} \begin{array}{l} \text{NMMe} \cdot \text{C}_6\text{H}_4\text{CO} \\ | \\ \text{NMMe} \cdot \text{C}_6\text{H}_4\text{CO} \end{array}$ , is formed when

hydrochloric acid is added to the dicyanogen compound; it separates out in greenish flocks, which, when crystallised from alcohol, form long, white branching needles, m.p.  $206$ — $207.5^\circ$ . Ammonia is formed at the same time. By boiling the alcoholic solution with concentrated hydrochloric acid, it is converted into diorthotolylparabanic acid,  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_3$ ; it crystallises from alcohol in small white, branching needles, m.p.  $202.5$ — $203.5^\circ$ . It is insoluble in water, sparingly in cold, but more soluble in hot alcohol, soluble in glacial acetic acid and carbon bisulphide, from the last solution it separates needles united in rosette-like groups. From an examination of the mother-liquors, it appears that ammonia, oxalic acid, and diorthotolylguanidine are formed.

*Triorthotolylguanidine*,  $(\text{C}_6\text{H}_7\text{Me} \cdot \text{NH})_2\text{C} : \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$ , obtained by treating an alcoholic solution of diorthotolylthiocarbamide with lead oxide in presence of orthotoluidine. It crystallises from alcohol in leaflets, or microscopic prisms, melting at  $130$ — $131^\circ$ . Its platinumchloride,  $(\text{C}_{22}\text{H}_{23}\text{N}_3 \cdot \text{HCl})_2\text{PtCl}_4$ , is a bright yellow, fine powder; and from alcohol it crystallises in tufts of prisms.

The  $\alpha$ -dicyano-derivative,  $\text{C}_{22}\text{H}_{21}\text{N}_3 + 2\text{CN}$ , has been obtained from the triorthotolylguanidine by evaporating its ethereal solutions, as a crust consisting of rounded masses formed of yellow needles, m.p.  $141^\circ$ ; when treated with hydrochloric acid, it yields *triorthotolylloxalylguanidine*,  $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_2$ , crystallising in yellow rhombic plates, m.p.  $179^\circ$ . In the preparation of this body, the formation of scarlet needles was observed, the nature of which is doubtful, but they may be the hydrochloride of  $\beta$ -dicyanotriorthotolylguanidine. This oxalyl-derivative, when boiled with hydrochloric acid for a long time, yields the diorthotolylparabanic acid.

By heating orthotoluidine hydrochloride with cyanamide in sealed tubes at  $100^{\circ}$  for some hours, diorthotolylcarbamide is obtained; it is insoluble in ether and water, and but sparingly in hot alcohol, from which it separates in light violet coloured needles, m. p.  $252^{\circ}$  (uncorr.). It is identical with the body obtained by Lachmann (*Ber.*, 12, 1350), by the decomposition of diocyanorthotolylchloride. By continued action of potash at  $150$ – $160^{\circ}$  it is resolved into carbonic anhydride and orthotoluidine.

In conclusion, the author states that the dinaphthylthiocarbamide described by Delbos (*Annalen*, 64, 371) and Schiff (*J. pr. Chem.*, 70, 271, and 71, 109), melts at  $197$ – $198^{\circ}$  (uncorr.), and is sparingly soluble in hot alcohol and hot glacial acetic acid. The attempts to prepare guanidine derivatives from this compound have not been successful.

P. P. B.

**Carbamides Derived from the Isomeric Toluidines.** By J. COSACK (*Ber.*, 12, 1449–1450).—The following have been prepared by the author:—

*Paratolylcarbamide*,  $\text{CO}(\text{NH}_2)\text{NH.C}_7\text{H}_7$ , from potassium cyanate and paratoluidine hydrochloride. Crystallises in thick needles; m. p.  $172^{\circ}$ . Already prepared by Sell (*Annalen*, 126, 158).

*Metatolylcarbamide*, prepared in a similar manner, crystallises from water in plates; m. p.  $142^{\circ}$ .

*Metaditolylcarbamide*,  $\text{CO}(\text{NH.C}_7\text{H}_7)_2$ , from metatoluidine and ethyl chlorocarbonate,  $2\text{C}_7\text{H}_7.\text{NH}_2 + \text{COClEt} = \text{CO}(\text{NH.C}_7\text{H}_7)_2 + \text{EtOH} + \text{HCl}$ ; crystallises from hot alcohol in brilliant colourless needles; m. p.  $217^{\circ}$ .

*Orthotolylurethane*,  $\text{CO}(\text{OEt})\text{NH.C}_7\text{H}_7$ , from orthotoluidine and ethyl chlorocarbonate. Crystallises from light petroleum in colourless tables; m. p.  $42^{\circ}$ . Described by Lachmann and by Merz (*Ber.*, 6, 444).

Ch. B.

**Action of Oxalic Acid on Carbazol.** By W. SUMA (*Ber.* 12, 1403–1406).—When carbazol is fused with ten to twelve times its weight of oxalic acid, the mixture becomes intensely blue; and by washing it with hot water and benzene, and extracting with hot alcohol, a blue substance may be obtained in microscopic crystals which show a coppery lustre when rubbed. This body has the composition  $\text{C}_{13}\text{H}_5\text{NO}$ , and is formed according to the equation—



It is insoluble in water, benzene, and petroleum ether, but soluble in alcohol and glacial acetic acid. Its solution in alcohol is precipitated by platinic chloride. Alkalis dissolve it, forming colourless solutions. Cold sulphuric acid also dissolves it: nitric acid colours it brown, and on heating dissolves it with carmine-red colour. Nitrous anhydride throws down a green precipitate from its solution in acetic acid.

Judging by its reactions and mode of formation, this body is best



regarded as an *internal anhydride* of *orthamidophenylbenzoic acid*,  

$$\begin{array}{c} \text{C}_6\text{H}_4\text{CO} \\ | \\ \text{C}_6\text{H}_4\text{NH} \end{array}$$
 Under the influence of various reagents it assimilates the elements of water, giving derivatives of the acid,



Thus alcohol precipitates the salt  $\text{C}_{13}\text{H}_{10}\text{NO}_2\text{K}$  from its solution in potash. Bromine converts it into a derivative,  $\text{C}_{13}\text{H}_8\text{Br}_3\text{NO}_2$ , and warm nitric acid converts it into a mixture of a dinitro- and a tetra-nitro - compound,  $\text{C}_{13}\text{H}_2(\text{NO}_2)_2\text{NO}_2$  and  $\text{C}_{13}\text{H}_7(\text{NO}_2)_4\text{NO}_2$ . Acetic anhydride, however, converts it into an insoluble compound,



When separated from its alkaline compounds, this body again parts with the elements of water just as isatic acid passes into isatin when set free from its salts.

Ch. B.

**Bromoxyl Derivatives of Benzene.** By R. BENNEDIKT (*Annalen*, 199, 127—138).—*Tribromophenol bromide*,  $\text{C}_6\text{H}_2\text{Br}_3\text{OBr}$ , is obtained by the action of excess of bromine-water on a dilute aqueous solution of phenol or salicylic acid (1 in 1,000) as a heavy yellow precipitate. As it is decomposed by alcohol, it must be purified by recrystallisation from boiling chloroform or carbon bisulphide. In this way, it is obtained in lustrous lemon-coloured plates which melt at  $118^\circ$  and decompose at  $125^\circ$ . The crystals are insoluble in ether and in water, they undergo no change on boiling with ammonia or with fixed alkalis. Tribromophenol bromide is converted into bromopicrin and picric acid by boiling with nitric acid, and is changed into tribromophenol by the action of warm alcohol. Tribromophenol is also produced when tribromophenol bromide is treated with tin and hydrochloric acid. Tribromophenol bromide dissolves in aniline with liberation of heat: on pouring the product of the reaction into a dilute solution of soda, and extracting with ether, tribromaniline is obtained, and tribromophenol remains in the alkaline aqueous solution. Tribromophenol bromide is transformed into tetrabromophenol (m. p.  $109^\circ$ ) when heated with sulphuric acid. By the action of heat alone, the phenol bromide loses an atom of bromine and leaves a resinous-looking substance which is probably hexabromophenoquinone,  $\text{C}_6\text{Br}_3\text{H}_2\text{O.O.C}_6\text{Br}_3\text{H}_2$ , but has not yet been obtained in the pure state. The author also points out that the chemical properties of pentabromoresorcinol may be best explained by the assumption that this substance is tribromoresorcinol bromide,  $\text{C}_6\text{Br}_3\text{H}(\text{OBr})_2$ .

W. C. W.

**Products of the Oxidation of the Ethers of Thymol.** By R. PATERNO and F. CANZONERI (*Gazzetta*, 9, 455—462). This paper gives the results obtained on treating the methyl and ethyl ethers of natural and of artificial thymol with dilute nitric acid.

When the methyl ether of natural thymol,  $\text{C}_8\text{H}_8\text{Me}(\text{C}_6\text{H}_7)\text{OMe}$ , is digested with dilute nitric acid (1 : 4) for several days, it is converted into a colourless crystalline substance which on analysis was found to be a *methoxynitrotoluic acid*,  $\text{C}_8\text{H}_5(\text{NO}_2)\text{Me}(\text{MeO}).\text{COOH}$ . It forms

very slender needles (m. p. 173—175°), very soluble in alcohol, ether, or benzene. Its barium salt may be obtained in straw-coloured crystals containing 2 mols.  $H_2O$ . Besides this, small quantities of methyl-metahomosalicylic and methoxyterephthalic acids seem to be formed. The corresponding ethyl compound of thymol (b.p. 227·8 at 756·7 mm.), when oxidised in a similar manner, yields *ethoxynitrotoluic acid* in long silky needles (m. p. 161—162°), *ethoxytoluic acid*,  $C_6H_5Me(EtO).COOH$  in minute quantity, and a third acid melting at 252—253°, and having all the characters of ethoxyterephthalic acid. From these experiments, taken in conjunction with the known difficulty of oxidising thymol by means of chromic mixture (*Gazzetta*, 5, 13), it would seem that the action of nitric acid first produces a nitro-derivative, which, being more easily oxidisable, is converted into the methoxy- or ethoxy-nitrotoluic acid.

The methyl ether of artificial camphothymol, when treated with dilute nitric acid in the manner above described, yields *methoxyterephthalic acid*,  $C_6H_5(MeO)(COOH)_2$ . It is a white crystalline powder consisting of minute prisms (m. p. 274—275°), only very sparingly soluble even in boiling water, but easily in alcohol: it is probably identical with Schall's acid (*Ber.*, 12, 828). The *ethyl ether of camphothymol*,  $C_6H_5Me(C_2H_7).OEt$ , prepared by treating the thymol with ethyl iodide and alcoholic potash in the usual way, is a colourless, transparent liquid of aromatic odour, and lighter than water. Its boiling point at 656·58 mm. is 228° (corr.), being almost identical with that of the corresponding derivative from natural thymol. When oxidised it yields *ethoxyterephthalic acid* in stellate clusters of minute white crystals. The acid melts at 253—254°, is almost insoluble in cold water, very sparingly soluble in ether or benzene, and but moderately soluble in alcohol.

It would seem that the synthetical thymol is more readily oxidised than the natural, and from this the author infers that in the synthetical camphothymol  $[CH_3 : OCH_3 : C_2H_7 = 1 : 2 : 4]$ , whilst in the natural thymol it is  $[CH_3 : OCH_3 : C_2H_7 = 1 : 3 : 4]$ . Attention is also drawn to the fact that the melting points of the *methoxy-acids* is higher than that of the corresponding *ethoxy-acids*. C. E. G.

**Formula of Quinhydrone.** By R. NIETZKI (*Ber.*, 12, 1978—1983).—A reply to Wichelhaus's remarks (*Ber.*, 12, 1500) on a previous communication of the author. The latter still maintains the correctness of his formula,  $C_{12}H_{10}O_4$ , for quinhydrone, and of his method for determining the amount of sulphurous acid necessary to convert a given weight of quinhydrone into hydroquinone, and thus settling the formula of the former compound. From an application of the same process to phenoquinone, he concludes that the latter is  $C_{18}H_{16}O_4$ . From these facts it would appear that quinone can unite with 2 mols. of a monatomic, or 1 mol. of a diatomic phenol. This is confirmed by the formation of a compound of quinone when resorcin and quinone in equal molecules are dissolved in warm benzene; if an excess of either be present it remains unacted on. *Resoquinone*,  $C_{12}H_{10}O_4$ , consists of almost black, dark red needles (m. p. about 90°); it is moderately soluble in alcohol and water, but less easily in cold benzene.

T. C.

**Amidomethylenecatechols.** By O. HESSE (*Annalen*, 199, 341—343).—*Amidomethylenecatechol hydrochloride*,  $C_7H_5(NH_2)O_2$ , is obtained in white crystals freely soluble in water and in alcohol, by the action of tin and hydrochloric acid on nitromethylenecatechol or on nitropiperonylic acid. In the latter case the following reaction takes place:— $C_8H_5(NO_2)O_4 + 3H_2 = C_7H_5(NH_2)O_2 + 2H_2O + CO_2$ . The aqueous solution of the hydrochloride gives a cherry-red coloration with ferric chloride, a precipitate and a blue coloration with excess of silver nitrate, and a purple coloration with chloride of gold. Platinum chloride throws down a pale-yellow crystalline precipitate.

The free base is an oily liquid soluble in ether, alcohol, and chloroform. The oxalate and sulphate form needle-shaped crystals soluble in water.

The dinitromethylenecatechol, obtained as a bye-product in the nitration of piperonylic acid (*Ann.*, 199, 75), yields a diamido-derivative on reduction. The hydrochloride of this base crystallises in white plates, which dissolve in strong sulphuric acid; on the addition of water the solution is coloured blue.

The aqueous solution of the hydrochloride is coloured green by ferric chloride, and reddish-brown by platinum chloride. The free base has not been obtained in the pure state. W. C. W.

**Behaviour of Hæmatoxylin on Destructive Distillation.** By R. MEYER (*Ber.*, 12, 1392—1393).—Baeyer has already pointed out the analogy between *gallein* (the phthalein of pyrogallol) and the colouring matters brasilin and hæmatoxylin. The composition of brasilin,  $C_{18}H_{14}O_6$ , and the fact that on destructive distillation it yields resorcinol, without a trace of pyrogallol, would point to its being a *resorcinol-succinein* isomeric with that artificially prepared by Baeyer. Hæmatoxylin,  $C_{18}H_{14}O_6$ , may then be a mixed succinein of pyrogallol and resorcinol; and the author has found that on destructive distillation it actually yields a mixture of these two phenols, easily recognised and separated as gallein and fluorescein. This view of the constitution of the two colouring matters does not account for the existence of the hexacetyl-hæmatoxylin described by Reim, and the tetracetyl-brasilin described by Liebermann and Burg. Both bodies require further examination. Ch. B.

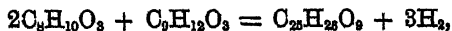
**Methylpyrogallol Acid and the Formation of Pittacal.** By A. W. HOFMANN (*Ber.*, 12, 1371—1385).—From former experiments (*Ber.*, 11, 329 and 1455) the author concluded that the colouring matters cedrret and pittacal, discovered by Reichenbach, were both derivatives of the dimethyl ether of pyrogallol. Pittacal, he found, was formed when the crude liquid dimethyl pyrogallate from beechwood tar was heated with caustic alkali and carbon sesquichloride. The two latter reagents when heated together yield oxalic acid, and it was therefore conjectured that pittacal was formed by the action of this acid on the pyrogallate, just as rosolic acid is formed by heating oxalic acid with phenol. Pittacal has in fact the composition of a hexamethoxylated rosolic acid,  $C_{18}H_8(OMe)_6O_7$ ; and this view of its constitution harmonises with the observations of Liebermann (*Ber.*, 9,

334), who describes it under the name *Eupittonic*. It has since been observed by the author, however, that neither of the two dimethyl-pyrogallol ethers extracted from beech-wood tar (by a process not yet published) yields any trace of pittacal by the above process. He also found that the crude ether when mixed with alkali and exposed to air, or better, heated in contact with it, yielded the blue colouring matter without the addition of any carbonaceous substance. The formation of pittacal must therefore be due to the presence of some third substance contained in the crude ether, which, bearing in mind the origin of rosaniline from aniline and toluidine, he suspected to be a homologue. Since this body could not be isolated by fractional distillation, the crude ether was treated with benzoic chloride, and the benzoyl compounds separated by crystallisation. He thus obtained the benzoyl derivatives of the dimethyl ethers of pyrogallol and propylpyrogallol, and finally a body melting at 118–119°, which, when decomposed by potash, yielded benzoic acid and dimethylmethyl pyrogallate,

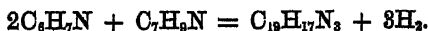


melting at 36° and boiling at 265°. Its constitution was proved by its yielding a dibrominated derivative (m. p. 126°) and the above-mentioned benzoyl derivative,  $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2.\text{OBz}$  (m. p. 118°). By heating with concentrated hydrochloric acid at 150–160°, it is resolved into methyl chloride and methylpyrogallol,  $\text{C}_6\text{H}_3\text{Me}(\text{OH})_3$ . This body (m. p. 129°) is soluble in water and volatilises unchanged. It bears a strong resemblance to ordinary pyrogallol, its alkaline solution turning brown on exposure to air.

The sodium derivatives of dimethyl pyrogallate and dimethyl methylpyrogallate are best obtained by adding soda to their alcoholic solutions. Separately, they may be heated in air without forming a trace of pittacal; but if a mixture of the two with excess of soda is heated, pittacal is formed, sometimes to the extent of 10 per cent. by weight of the mixed ethers. On treating it with water, the mass dissolves forming a deep indigo-blue solution. On adding hydrochloric acid the solution becomes carmine-red, and deposits a resinous mass which when purified furnishes eupittonic acid (pittacal) in beautiful crystals. The pittacal may also be extracted from the acidified solution with boiling benzene, unaltered pyrogallate having been first removed by agitation with ether. The quantity of colouring matter formed is not increased by the addition of oxidising agents, chiefly on account of the extreme ease with which these convert dimethyl pyrogallate into cedret. The reaction may be thus represented—



and may be compared with that by which rosaniline is produced—



In the former case the oxygen necessary to remove hydrogen is derived from the atmosphere, as may be proved by attempting to conduct the reaction out of contact with air.

Eupittonic acid appears to be bibasic. Salts of it with the alkaline and alkaline-earthly metals, ammonium, copper, nickel, cobalt, lead

and zinc, have been prepared. The alkaline salts are blue with green reflexion. The ammonium compound is decomposed when its solution is boiled, and after a time crystals of pittacal are deposited.

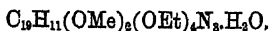
In virtue of the deep blue colour of the alkaline compounds of pittacal, paper steeped in a solution of it and dried, furnishes an exceedingly sensitive test for free alkalis. Unfortunately concentrated hydrochloric acid also colours it blue.

When boiled with acetic anhydride, eupittonic acid yields a yellow diacetyl-derivative, which strangely enough is insoluble in alkalis, although its molecule ought still to contain four hydroxyl groups.

The triamine  $C_{25}H_{28}N_3O_8 \cdot H_2O$ , previously described (*loc. cit.*), is obtained with surprising ease from eupittonic acid. Its salts give pure blue solutions and might be used as dyes.

A homologue of eupittonic acid,  $C_{28}H_{34}O_8$  (which was not analysed), was prepared by heating *diethyl pyrogallate* and *dimethyl methylpyrogallate* with soda.

It differs from its prototype in being soluble in ether and less easily crystallisable, and in the less stability of its ammonium compound. It also forms a triamine when heated with ammonia, probably a *dimethozyl-tetretrozyl-pararosaniline*,



The salts of this base are blue.

Ch. B.

**Ethylene Ether of Pyrogallol.** By G. MAGATH (*Ber.*, 12, 1860—1863).—This ether is prepared by heating 2 mols. pyrogallol, 3 mols. ethylene bromide, and 6 mols. potash with ethyl alcohol at  $100^\circ$  for 15—20 hours: the ether is obtained from the product by acidifying with hydrochloric acid and extracting with ether. The ethereal extract on rectification yielded the monethylene pyrogallate, as a colourless, heavy, strongly refractive liquid of a burning taste, and having the odour of beech-wood tar; it boils at  $267^\circ$ .

Its analysis and vapour-density determination show its formula to be  $C_6H_3(OH):O_3:C_2H_4$ . It resembles the phenols in its properties, forming crystalline compounds with alkalis, benzoic chloride, and bromine.

The benzoyl compound,  $C_8H_7O_3Bz$ , is a white crystalline substance, easily soluble in boiling alcohol and ether (m. p.  $109^\circ$ ). The bromo-compound crystallises from glacial acetic acid in transparent tables (m. p.  $67^\circ$ ).

A compound, which is insoluble in alkalis, is formed at the same time as the ethylene ether; it is soluble in alcohol and ether, and from the former is obtained in ill-defined crystals (m. p.  $88^\circ$ ). It appears to have the composition  $C_{10}H_{11}O_3Br$ .

Monethylene pyrogallate is easily oxidised by ferric chloride and potassium dichromate; the oxidation-product is, however, apparently not uniform in composition. It is not dissolved but blackened by sulphuric acid, and therefore differs from the class of compounds to which cediret belongs.

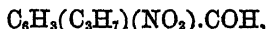
By the oxidation of diphenol,  $C_{12}H_8(OH)_2$  (m. p.  $270^\circ$ ) with potassium dichromate and acetic acid, a compound is obtained which dis-

solves in sulphuric acid, forming a beautiful blue solution, a characteristic property of cedriret. The author is engaged with the further study of this reaction.

P. P. B.

**Nitrocuminaldehyde and its Derivatives.** Part II. By E. LIPPMANN and W. STRECKER (*Wien Akad. Ber.*, 78, 570—572).—With a view of obtaining a nitrocuminaldehyde in which the  $\text{NO}_2$  should take the place of hydrogen in a fatty group, similar to the two isomerides,  $\text{C}_6\text{H}_5(\text{NO}_2).\text{COH}$  and  $\text{C}_6\text{H}_5.\text{C}(\text{NO}_2)\text{OH}$ , previously obtained by the nitration of benzaldehyde, the latter of which yields benzoic and nitric acids on oxidation, the authors have prepared pure cuminaldehyde from the commercial article by treatment with hydrogen sodium and sulphite, &c. It boils at  $217^\circ$  (corr.  $222^\circ$ ), and may be nitrated by dropping it into a cooled mixture of nitric and sulphuric acids, and subsequently washing with soda solution; a crystalline body is thus obtained, together with an oil, easily removable by alcohol, in which the crystals are insoluble.

The crystalline substance is a nitrocuminaldehyde,



and gives a compound with sodium hydrogen sulphite, after separation, from which it forms sulphur-yellow crystals melting at  $54^\circ$ , and exhibiting a tendency to remain liquid after fusion.

According to Ditscheiner the crystals are doubly oblique prisms.

On oxidation with chromic mixture, a nitrocuminic acid is formed (m. p.  $158^\circ$ ), identical with the acid obtained by nitration of cuminic acid,  $\text{C}_6\text{H}_5(\text{NO}_2)(\text{C}_2\text{H}_5).\text{COOH}$ , and probably it crystallises in oblique prisms—

$$a : b : c = 1.57133 : 1 : 1.26742.$$

On reduction, it gives an amido-acid forming a hydrochloride identical with the one described by Cahours (*Annalen*, 109, 10).

As a mixture of two amido acids was obtained by Paternò and Fileti (*Gazzetta*, 5, 383) by reduction of nitrocuminic acid, the authors intend to examine the reaction more carefully to ascertain if the nitration products from the aldehyde contain two isomerides.

W. R. H.

**Fittica's Nitrobenzoic Acids.** By C. BODEWIG (*Ber.*, 12, 1983 1984).—The author has examined the physical properties of the four nitrobenzoic acids described by Fittica (*J. pr. Chem.*, 1878, 184).

The acid (m. p.  $127^\circ$ ) separates from solution in acetone as an unstable  $\alpha$ -modification of the meta-acid (m. p.  $142^\circ$ ). This  $\alpha$ -modification forms monosymmetrical crystals (m. p.  $141^\circ$ ).

The meta-acid on crystallisation from a mixture of alcohol and ether or from acetone, gives an unstable  $\beta$ -modification and a stable  $\gamma$ -modification, both of which are monosymmetrical.

The nitro-acid (m. p.  $136^\circ$ ) on crystallisation from acetone gives the stable  $\gamma$ -modification of the meta-acid. The lemon-yellow acid (m. p.  $142^\circ$ ) under similar circumstances is converted into the unstable  $\beta$ -modification.

The ethers of the meta-acid (m. p.  $142^\circ$ ), of the acid m. p.  $127^\circ$ ,

and of the lemon-yellow acid (m. p.  $142^{\circ}$ ), are identical as regards their physical properties.

Measurements of the above crystals are given.

T. C.

**Xylic Acid, its Preparation and Derivatives.** By E. ADOR and F. MEIER (*Ber.*, 12, 1968—1971).—The most ready method for preparing xylic acid [ $\text{COOH} : \text{CH}_3 : \text{CH}_3 = 1 : 2 : 4$ ] (m. p.  $120^{\circ}$ , b. p.  $267^{\circ}$ , bar. 727 mm.) is by passing a current of carbon oxychloride into pure [1 : 3] xylene in presence of an excess of aluminium chloride, and occasionally heating to  $100^{\circ}$ , thus:— $\text{C}_8\text{H}_8\text{Me}_2 + \text{COCl}_2 = \text{C}_8\text{H}_8\text{Me}_2\text{COCl} + \text{HCl}$ . The chloride thus produced gives the acid on decomposition with water. The barium, calcium, ammonium, and silver salts were prepared and described.

*Xylylic chloride*,  $\text{C}_8\text{H}_8\text{Me}_2\text{COCl}$  is obtained by treating the acid with phosphorus pentachloride. It is a colourless liquid (b. p.  $235^{\circ}$ ), which on cooling crystallises in needles (m. p.  $25^{\circ}$ ).

*Xylylamide*,  $\text{C}_8\text{H}_8\text{Me}_2\text{ONH}_2$ , was prepared by triturating the preceding compound with ammonium carbonate. It is almost insoluble in cold water, and separates from the hot solution in needles (m. p.  $181^{\circ}$ ), which are very soluble in alcohol. After sublimation it melts at  $179^{\circ}$ . This amide is a very stable body, not being decomposed by soda even on boiling; it is, however, readily acted on by hydrochloric acid with reproduction of xylic acid. It dissolves in acids, forming somewhat unstable salts. The *anilide*, obtained by adding the chloride gradually to aniline, consists of crystals (m. p.  $138^{\circ}$ ), which are but sparingly soluble even in hot water, but more easily in alcohol. On boiling with hydrochloric acid, it is partially decomposed.

T. C.

**Parahydroxyphenylacetic Acid.** By H. SALKOWSKI (*Ber.*, 12, 1438—1441).—Amongst the putrefaction products of horn, the author and his brother (*Ber.*, 12, 648) found a *hydroxyphenylacetic acid* different from those previously known. This acid now proves to be identical with hydroxyphenylacetic acid, obtained synthetically by the author in the following way:—Phenylacetic acid is nitrated, the isomeric para- and ortho-nitro-compounds formed (Radziszewski, *ibid.*, 2, 207, and 3, 648) are reduced, and the amido-acids separated by Baeyer's method (*ibid.*, 11, 583). The *paramidlophenylacetic acid* (which has already been described by Radziszewski) was easily converted into the hydroxy-acid by boiling with potassium nitrite and dilute sulphuric acid.

*Parahydroxyphenylacetic acid* crystallises in brittle, flat, prismatic needles (m. p.  $148^{\circ}$ ), which are very soluble in water, alcohol, and ether, and may be volatilised unchanged. With ferric chloride it gives a grey-violet colour, rapidly changing to dirty green. Its ammonium salt is soluble and crystallisable; its solution gives no precipitate with zinc, cadmium, or cupric sulphates. The silver salt is soluble in, and crystallisable from, boiling water. Lead and calcium salts have also been prepared. The ethyl salt is an oily liquid; by heating it with ethyl iodide and potash, and saponifying, *ethoxyphenylacetic acid* has been obtained (m. p.  $88^{\circ}$ ).

Parahydroxyphenylacetic acid yields paracresol when distilled with soda-lime. It is produced during the putrefaction of serum albumin as well as of horn.

Ch. B.

**Paramethoxyphenylcinnamic Acid and Methoxystilbene.** By A. OGIALORO (*Gazzetta*, 9, 533—537).—On heating a mixture of 17 parts of anisaldehyde with 20 of sodium phenylacetate and 70 of acetic anhydride for 8 hours at 150° a crystalline mass is obtained, which, after being boiled with water, is treated with excess of solution of sodium carbonate; this leaves undissolved a small quantity of methoxystilbene, whilst the filtered solution, after being twice washed with ether, yields a precipitate of *paramethoxyphenylcinnamic acid*,  $\text{OMe.C}_6\text{H}_4.\text{CH.CPh.COOH}$ , on addition of hydrochloric acid. It may readily be purified by crystallisation from boiling absolute alcohol, when it is deposited in hard yellowish prisms if the solution is not too concentrated. The acid is but moderately soluble in ether, and only very sparingly in water, as are also the greater number of its salts. Although it is dissolved but slowly by sodium carbonate solution, ammonia and solutions of potash or soda dissolve it readily. Heated with a hot saturated solution of barium hydroxide, it yields the barium salt, but at the same time a portion of the acid loses the elements of carbonic anhydride and becomes converted into methoxystilbene. Its acid properties are relatively feeble, the ammonium and barium salts being decomposed by a current of carbonic anhydride. The acid melts at 188—189°, but at a somewhat higher temperature it is decomposed, splitting up sharply into carbonic anhydride and methoxystilbene, which distils over.

*Methoxystilbene*,  $\text{OMe.C}_6\text{H}_4.\text{CH.CPh}$ , which, as just stated, may be readily prepared by distilling the methoxyphenylcinnamic acid, is insoluble in water, but dissolves easily in ether and in hot alcohol, crystallising out in exceedingly thin micaceous scales (m. p. 136°). From its constitution and formula, it will be seen that this compound is the methyl ether of a phenolic compound, which may be termed *stilbophenol*.

As no reaction takes place between benzaldehyde, cadmium paratoluate and acetic anhydride, it would seem necessary that the acid should contain the group  $\text{CH}_2.\text{COOH}$ , as is the case with all the acids which have yielded successful results hitherto. The author hopes to be able to definitively establish this hypothesis by further experiments.

C. E. G.

**Metaisatic Acid (Metamidophenylglyoxylic Acid).** By L. CLAISEN and C. M. THOMPSON (*Ber.*, 12, 1942—1948).—This is an account of the application of the reaction (*Ber.*, 12, 350) by which nitrobenzoic acid was converted into isatin, to the corresponding meta-compound. Metanitrobenzoic chloride was first prepared from metanitrobenzoic acid by heating the latter with an equivalent quantity of phosphorus pentachloride and distilling off the phosphorus oxychloride formed. Metanitrobenzoic chloride thus obtained crystallises in brilliant rhombic pyramids (m. p. 33°, b. p. 184°, under a pressure of about 50—55 mm.), and on distillation over silver cyanide yields the corresponding cyanide as a thick yellow liquid (b. p. 281° under a pressure of about 145 mm.) which does not solidify at -17°. This dissolves in concentrated potash with formation of potassium nitrobenzoate and potassium cyanide. On long standing in contact with strong hydrochloric acid, it is converted into a mixture of metaisat-



amide,  $C_6H_4(CO.CO.NH_2).NO_2$  (1:3), and nitrobenzoic acid. The former consists of white or slightly yellow prisms (m. p.  $152^\circ$ ), sparingly soluble in cold water, only moderately in ether, but easily soluble in alcohol, chloroform, benzene, and boiling water.

*Meta-isatic acid*,  $C_6H_4(CO.COOH).NO_2 = [1:3]$  was obtained from the above amido-acid in the usual way. It crystallises in prisms (m. p.  $78^\circ$ , with previous intumescence at about  $65^\circ$ ), and like phenylglyoxylic acid gives, when treated with benzene and sulphuric acid, an intense carmine and afterwards a violet-red colour, but is characterised (and also its salts) by a far more bitter taste. The potassium, barium,  $(C_6H_4NO_2)_2Ba + H_2O$ , silver, and ethyl salts were prepared. Meta-isatic acid was converted into the corresponding amido-acid,  $C_6H_4(CO.COOH).NH_2$ , by reducing the alkaline solution of the acid with ferrous sulphate. It is a strong acid and crystallises in colourless prisms and needles, which, when heated, are first discoloured and afterwards partially melt at  $270-280^\circ$ , and are not completely volatile at  $300^\circ$ . It is sparingly soluble in cold, but more easily in hot water, and is practically insoluble in alcohol, ether, benzene, and chloroform. The barium and silver salts were prepared. The hydrochloride,  $C_6H_4(CO.COOH).NH_2.HCl$ , forms groups of prisms, and gives with platinic chloride a precipitate of the platinochloride. T. C.

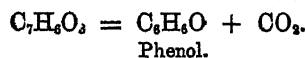
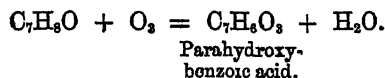
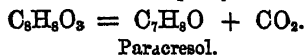
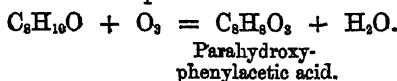
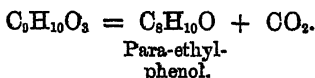
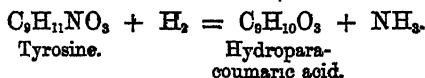
**Formation of Hydroparacoumaric Acid from Tyrosine.** By E. BAUMANN (*Ber.*, 12, 1450—1454).—In conjunction with Brieger, the author has already shown (*Zeit. Phys. Chem.*, 1, 60) that paracresol and a little common phenol are produced during the putrefaction of albumin. The former is in all probability a decomposition-product of tyrosine, which Weyl has proved to yield these phenols by putrefaction (*Ber.*, 12, 354). The author has also proved that paracresol, when administered to dogs, appears in the urine partly as parahydroxybenzoic acid (*Zeit. Phys. Chem.*, 3, 250) chiefly as paracresolsulphonic acid (*ibid.*, 1, 244). Parahydroxybenzoic acid is decomposed partly by digestion (*ibid.*, 3, 250), wholly by putrefaction (*ibid.*, 1, 60) into phenol and carbonic anhydride. To establish the connection between phenol and tyrosine, it only remained then to trace the changes by which paracresol is produced from it.

Six grams of pure tyrosine were mixed with five liters of water and a little putrefying pancreas and exposed to air for two days in an incubator. The tyrosine had then been completely dissolved, and by concentrating the filtered liquid, acidifying with sulphuric acid and extracting with ether, *hydroparacoumaric acid* was obtained. This change is evidently of the same kind as the formation of succinic acid from aspartic acid by fermentation, and furnishes an additional proof that tyrosine belongs to the paracresol series (Barth, *Annalen*, 136, 110; 152, 96; and 163, 296), although Barth failed to obtain it synthetically.

From fresh concentrated urine also, ether extracts an acid which gives Plugge's phenol-reaction (*Zeit. Anal. Chem.*, 1872, 173), and after this has been removed and the urine boiled with hydrochloric acid as long as phenol is given off, a similar acid may again be extracted by ether. These acids are probably identical with, or related to, hydroparacoumaric acid.

The series of phenol-derivatives obtained by the putrefaction of albumin (tyrosine) has been rendered complete by the author's discovery (*Ber.*, 12, 1438) of *parahydroxyphenylacetic acid* amongst the products from putrefying horn.

The several stages of the conversion of tyrosine into phenol may be thus represented :—



Of these bodies, paraethylphenol and parahydroxybenzoic acid alone have not been traced directly to albumin or tyrosin.

Such a series of changes is quite in accordance with Hoppe-Seyler's theory of fermentation and its connection with vital processes (*Pflüger's Arch.*, 12, 1). Similar oxidations and reductions have been effected by Tiemann in the protocatechuic series (*Ber.*, 11, 659). Ch. B.

**Californian Orcella Weed.** By O. HESSE (*Annalen*, 199, 338—341).—This lichen, which is a variety of *Roccella fuciformis*, contains erythrin and a small quantity of roccellic acid. An alcoholic solution of erythrin has no action on polarised light. W. C. W.

**Products of the Dry Distillation of Calcium Phthalate.** By O. MILLER (*Ber.*, 12, 1489—1490).—By this operation, the author has obtained benzene, benzophenone, a crystalline compound (m. p. 145.5—146°), apparently identical with Hemilian's diphenylene-phenylmethane, and a body (m. p. 243—244°) having the properties of the hydrocarbon  $C_{13}H_{10}$ , which Thörrer and Zincke prepared by acting on  $\alpha$ -benzopinacene with soda-lime; the two latter in very small quantity. The first three of these are also obtained by distillation of calcium benzoate, from which it might be inferred that this salt is produced during the distillation of calcium phthalate; the author, however, was unable to detect it. The object of his research was to obtain the ketone  $C_6H_4 : CO$ ; the fact that he did not succeed confirms Kekulé's view concerning the non-existence of benzene derivatives containing the group  $(C_6H_4)''$  united with an elementary atom. The author is studying the distillation-products of calcium succinate.

Ch. B.

**Toluenemonosulphonic Acids.** By P. CLAUSSON and K. WALLIN (*Ber.*, 12, 1848—1854).—On treating toluene cooled to  $10^{\circ}$  with sulphuric chloride, the following reaction takes place,  $2C_6H_5 + 3(HO.SO_2Cl) = C_6H_7.SO_2Cl + C_6H_7.SO_3H + H_2SO_4 + 2HCl$ . The sulphonic chlorides were separated from the rest by pouring the product into ice-cold water, and from the mixed sulphonic chlorides, the solid paratoluenesulphonic chloride separated on standing, and by cooling to  $-20^{\circ}$ , leaving the liquid chlorides. From the aqueous solution, the potassium salts of the sulphonic acids were prepared, and these again converted into the chlorides by means of phosphorus pentachloride, and the solid para-compound separated as before. The fluid chlorides were converted into the corresponding amides, from which, by fractional crystallisation, the ortho-amide and meta-amide were obtained. This method of separation was proposed by Beckurts (*Ber.*, 10, 943) and Fahlberg (*ibid.*, 12, 1048), and the melting points of the derivatives agree with those given by Fahlberg (*loc. cit.*) and Müller (*ibid.*, 12, 1348). From tolueneparasulphonic chloride, after

|                 | Para-series.  | Meta-series.   | Ortho-series.  |
|-----------------|---|--|--|
| Acids.....      | $C_6H_7.SO_3H + H_2O$ .<br>Crystallises better than the isomerides. Long thick leaflets, or flat prisms. Deliquescent.  | $C_6H_7.SO_3H + H_2O$ .<br>Thin crystalline scales. Very soluble and deliquescent.   | $C_6H_7.SO_3H + 2H_2O$ .<br>Thin leaflets. Very easily soluble. Deliquescent.  |
| Potassium salts | $C_6H_7.SO_3K + H_2O$ .<br>Long prisms, like nitre. Soluble.  | $C_6H_7.SO_3K + H_2O$ .<br>Needles or thin plates, united to form nodules. Very easily soluble.  | $C_6H_7.SO_3K + H_2O$ .<br>Tables of rhombic or almost quadratic habit. Soluble.   |
| Calcium salts   | $(C_6H_7.SO_3)_2Ca + 4H_2O$ .<br>Crystallises well in apparently monochinic prisms. Easily soluble.   | $(C_6H_7.SO_3)_2Ca + 3H_2O$ .<br>Long fine needles; very easily soluble.   | $(C_6H_7.SO_3)_2Ca$ .<br>Separates from its solutions on cooling, in leafy crystals.   |
| Zinc salts ..   | $(C_6H_7.SO_3)_2Zn + 6H_2O$ .<br>Crystallises in quadratic acuminate prisms. Easily soluble.  | $(C_6H_7.SO_3)_2Zn + 7H_2O$ .<br>Rectangular, thin leaflets. Easily soluble.   | $(C_6H_7.SO_3)_2Zn + 7H_2O$ .<br>Large prisms. Easily soluble.   |
| Amides ....     | $C_6H_7.SO_2NH_2$ .<br>Crystallises from water and alcohol in leaflets. Sparingly soluble in water; more so in alcohol. 1 pt. amide in 515 pts. of water at $4^{\circ}$ , or in 13.5 pts of alcohol at $5^{\circ}$ . M. p $136^{\circ}$ . | $C_6H_7.SO_2NH_2$ .<br>Crystallises from alcohol and water in long, leafy forms. Sparingly soluble in water; more so in alcohol. 1 pt. amide in 248 pts. water at $9^{\circ}$ , or in 5.7 pts. of alcohol at $5^{\circ}$ . M. p. $107-108^{\circ}$ . | $C_6H_7.SO_2NH_2$ .<br>From water and alcohol in quadratic octahedrons and prisms. Insoluble in cold water; sparingly soluble in alcohol. 1 pt. amide in 958 pts. water at $9^{\circ}$ , or in 28 pts. of alcohol at $5^{\circ}$ . M. p. $153-154^{\circ}$ . |

crystallisation from ether, the acid was obtained by boiling with water, and the corresponding acid from toluene ortho-sulphonamide by heating it with hydrochloric acid at 135–140°, and in a similar manner at 150°, the toluenemetasulphonic acid was obtained from the toluenemetasulphonamide. The authors have by this means obtained excellent yields of the above compounds; whilst Beckurts and Otto (*ibid.*, 11, 2061) found the para-derivative to be the chief and almost the only product of the action of sulphuric chloride on toluene. A table is given containing the results of the comparative study of the three isomeric toluenesulphuric acids, from which the foregoing (p. 256) are taken.

From these results, the authors conclude that the metatoluenesulphonic acid is not, as supposed by Fahlberg, a mixture of the para- and ortho-acids. Further, the ortho- and meta-acids may be separated by means of the barium, calcium, or silver salts, as well as by their amides. The properties attributed to the salts of the ortho- and metatoluenesulphonic acids, prepared indirectly from bromo-, nitro-, and amido-toluenes, do not agree with the above descriptions.

P. P. B.

**Oxidation-products of Cymene-sulphonamide.** By L. B. HALL and I. REMSEN (*Ber.*, 12, 1432–1436).—It has been previously shown that when xylenesulphonamide is oxidised, it yields sulphonamidometatoluic acid and some sulphonamidoparatoluic acid. The former acid has been partially examined by Iles and Remsen (*Ber.*, 11, 229), who converted it into paratoluic acid by treatment with hydrochloric acid.

*Sulphonamidoparatoluic acid* is also readily furnished by oxidation of cymenesulphonamide [ $\text{CH}_3 : \text{C}_6\text{H}_5 : \text{SO}_2\text{NH}_2 = 1 : 4 : 2$ ]. The group  $\text{SO}_2\text{NH}_2$  appears to protect the methyl (ortho-) group from oxidation, the propyl being converted into carboxyl.

By fusion with potash, this acid is converted first into the  $\alpha$ -oxy-paratoluic acid of v. Gerichten and Rossler (*Ber.*, 11, 1586), which is further oxidised to the oxyterephthalic acid of Burkhardt (*Ber.*, 10, 144). The first of these acids crystallises from hot water in needles, does not volatilise with steam, and gives no colour with ferric chloride. Its lead salt was prepared and analysed.

By oxidising sulphonamidometatoluic acid with potassium permanganate, Remsen and Iles obtained sulphonisophthalic acid. When free sulphonamidoparatoluic acid is similarly oxidised, it yields a salt,  $\text{C}_6\text{H}_4(\text{COOH})_2\text{SO}_3\text{K} + \text{H}_2\text{O}$ , presumably of *sulphonterephthalic acid*, still containing two displaceable hydrogen atoms. But when the corresponding potassium salt is treated with permanganate instead of the free acid, the result is different. Very little ammonia is evolved, and a salt having the constitution,  $\text{C}_6\text{H}_4(\text{COOK})_2 < \text{SO}_2 > \text{NH} + \text{H}_2\text{O}$ , is the principal product. The molecule of water is given off at 240°; it is probably not constitutional. On this view, the free acid, *anhydrosulphonamido-terephthalic acid*, would be analogous to the anhydro-compound,  $\text{C}_6\text{H}_4 < \text{SO}_2 > \text{NH}$ , obtained by the oxidation of ortho-toluenesulphonamide (Remsen and Fahlberg, *Ber.*, 12, 469). If, how-

ever, the water given off at 240° be constitutional (see next Abstract), the salt will have the formula,  $C_6H_3(COOK)(COOH).SO_2NH_2$ .

Ch. B.

**Anhydrosulphonamidoisophthalic Acid.** By I. REMSEN and R. D. COALE (*Ber.*, 12, 1436—1438).—According to Remsen, when sulphonamidometatoluic acid is treated with potassium permanganate, it yields only sulphonisophthalic acid; while Jacobsen asserts that sulphonamidoisophthalic acid is the product. In the authors' opinion, this latter acid cannot exist, since on being set free it is at once converted into an anhydride. This anhydro-acid (m. p. 283·5°) is obtained by oxidising sulphonamidometatoluic acid in *strongly alkaline* solution with permanganate on the water-bath, and acidulating the filtered and decolorised solution with hydrochloric acid. Its potassium salt,  $C_6H_3(COOK)<\frac{SO_2}{CO}>NH + 2H_2O$ , may be formed by cautiously adding hydrochloric acid to its solution in potassium carbonate. As proved by titration, this salt is capable of taking up an additional atom of base.

The authors conclude that a sulphonamide and a carboxyl group cannot exist together in the ortho-position, but may in the meta- or para-position.

Ch. B.

**Solubility of some Constituents of Coal-tar.** By G. v. BECHI (*Ber.*, 12, 1976—1978).

|  | 100 parts of Toluene dissolve |                    | 100 parts of absolute Alcohol dissolve |                    |
|--|-------------------------------|--------------------|--|--------------------|
|  | At the ordinary temperature.  | At 100°.           | At the ordinary temperature.           | At 78°.            |
| Naphthalene....  | 31 94                         | In all proportions | 5·29                                   | In all proportions |
| Anthracene ....  | 92                            | 12 94              | ·076                                   | ·83                |
| Phenanthrene...  | 33 02                         | In all proportions | 2·62                                   | 10·08              |
| Pyrene.....  | 16 54                         | Very soluble       | 1 37                                   | 3·08               |
| Chrysene.....  | 24                            | 5·39               | ·097                                   | ·17                |
| Carbazol.....  | 55                            | 5·46               | ·92                                    | 3·88               |
| Phenyl-naphthyl-carbazol,<br>C <sub>16</sub> H <sub>11</sub> N | Scarcely soluble              | ·39—·57            | Scarcely soluble                       | ·25                |
| Anthraquinone..  | ·19                           | 2·56               | ·05                                    | 2 25               |

T. C.

**Skatole.** By L. BRIGER (*Ber.*, 12, 1985—1988).—This compound, which was previously obtained by the author (*Ber.*, 10, 1027) from human excrement, crystallises in brilliant white plates (m. p. 93°), and has an intense faecal odour. It has great resemblance to indole, from which it differs, however, in being much less soluble in water, in having a higher melting point, in its odour, and also in the fact that it does not give a coloration with chlorine-water, or a red precipitate with

fuming nitric acid, but only a white cloud. On warming with dilute nitric or hydrochloric acid, it assumes a violet colour. An analysis gave numbers which were the mean of those required by the formulæ  $C_{10}H_{10}N$  and  $C_{10}H_{11}N$ . An analysis by Nencki (*Centr. Med. Wissenschaft*, 1878, No. 47) of the same substance obtained by the fermentation of flesh in the presence of pancreas infusion, led to the formula  $C_9H_9N$ . The best method for preparing skatole is by the fermentation of blood-albumin with a little pancreas and water, indole being also formed at the same time. Several analyses of the skatole thus obtained gave numbers corresponding with the formula  $C_9H_9N$ , and a vapour-density determination gave 65.2 instead of 65.5.

Administered in small doses, skatole appears to have no deleterious effect on the animal system, but in larger quantities it produces tetanus. An examination of the urine showed that the proportion of ethylsulphates to sulphates had considerably increased. T. C.

**Peculiar Formation of Tolane Tetrachloride.** By C. LIEBERMANN and J. HOMEYER (*Ber.*, 12, 1971—1976).—Tolane tetrachloride was obtained as a bye-product in the preparation of a large quantity of benzotrichloride by the action of chlorine on boiling toluene. It crystallises in rhombic prisms (m. p.  $163^\circ$ ), and is remarkable for its great stability, not being attacked by boiling nitric acid, nor by a mixture of chromic and acetic acids, nor on heating the alcoholic solution with oxide of silver or with potash. On heating with dimethylaniline and zinc chloride, it gives a violet colour. The author confirms Zinin in the observation that tolane tetrachloride gives two isomeric dichlorides,  $C_{14}H_{10}Cl_2$ , when its alcoholic solution is boiled with zinc. The compound least soluble in alcohol crystallises in rhombic tables (m. p.  $143^\circ$ ;  $153^\circ$ , Zinin; also Limpricht and Schwanert, *Ber.*, 4, 379), and the other in needles (m. p.  $63^\circ$ ). Tolane tetrachloride in alcoholic solution gives tolane (v. d. = 6.34, calculated for  $C_{14}H_{10}$  = 6.18) on treatment with sodium amalgam, thus confirming the earlier observations of Zinin; stilbene and dibenzyl are also formed at the same time. Tolane, on oxidation with chromic mixture, gives benzoic acid, and when its solution in chloroform is treated with chlorine the chloride (m. p.  $143^\circ$ ) is obtained. Tolane dibromide,  $C_{14}H_{10}Br_2$  (m. p.  $207^\circ$ ;  $205^\circ$  according to Limpricht and Schwanert), is produced by the action of an excess of bromine on a solution of tolane in carbon bisulphide. Stilbene is obtained when tolane tetrachloride is heated with zinc-dust, and benzil when the same substance is acted on by glacial acetic acid for a long time at  $230$ — $250^\circ$ , or by concentrated sulphuric acid at  $165^\circ$ , small quantities of benzoic acid being produced at the same time. T. C.

**Synthesis of Diphenylpropane: New Method of Forming Dibenzyl.** By R. D. SILVA (*Compt. rend.*, 89, 606—608).—By acting with ordinary propylene dichloride on benzene in presence of aluminium chloride according to the method suggested by Friedel and Crafts, diphenylpropane is obtained as a slightly viscid liquid of agreeable odour, boiling without decomposition between  $277^\circ$  and  $279^\circ$ .

Its density is 0.9256 at 0°. The same hydrocarbon is obtained when allyl chloride is substituted for propylene chloride; it is most likely, therefore, that the allyl-benzene combines with the liberated hydrochloric acid to form the compound  $C_6H_5.CH_2.CHCl.CH_3$ , which afterwards reacts with the excess of benzene to form diphenylpropane.

Ethylene dichloride reacts in a similar manner with benzene and aluminium chloride, forming diphenylethane, which should be identical with dibenzyl. This was proved to be the case by comparing its reactions with that of dibenzyl prepared by the action of finely divided silver on benzyl iodide. The melting points of both compounds was 52.5°, and their boiling points 276—277°. Diphenylethane crystallises from an ethereal solution in prisms belonging to the orthorhombic type.

J. W.

**Di- and Tri-derivatives of Naphthalene.** By R. MELDOLA (*Ber.*, 12, 1961—1965).—A continuation of the author's previous work on this subject.

*$\alpha\beta$ -Dibromonaphthylamine*,  $C_{10}H_7Br_2N$ , is obtained by heating dibromacetonephthalide with concentrated soda-lye at 140—150° for several hours. It crystallises in large white needles (m. p. 118°), which are easily soluble in benzene, petroleum, alcohol, ether, and chloroform; it has no basic properties. On oxidation with chromic and acetic acids, it gives an evanescent indigo-blue coloration, and by oxidation with dilute nitric acid, it yields phthalic acid, showing that the bromine and amido-groups are all in the same benzene ring, and since Rother and Liebermann have shown that in bromacetonephthalide the bromine atom and the  $NH.C_2H_5O$  group occupy the position (1:4), it is probable that in the new dibromonaphthylamine the arrangement is  $NH_2 : Br : Br = 1 : 2 : 4$ .

*$\alpha\beta$ -Dibromonaphthalene* was obtained from the preceding compound by means of the diazo-reaction. It crystallises in white needles (m. p. 64°). From considerations based on the lowness of this melting point as compared with that of the isomeric  $\beta$ -compound (m. p. 81°) prepared by Glaser and afterwards by Jolin (*Bull. Soc. Chim.* [2], 28, 514), the author concludes that it is a meta-compound, as we should have expected from the constitution above ascribed to  *$\alpha\beta$ -dibromonaphthylamine*.

*$\alpha$ -Bromonaphthalenesulphonic acid*, obtained by the action of fuming sulphuric acid on  *$\alpha$ -bromonaphthalene*, gives phthalic acid on oxidation with an alkaline solution of potassium permanganate, thus proving it to have the constitution  $HSO_3 : Br = 1 : 4$ .

Sodium bromonaphthalenesulphonate on fusion with soda does not give bromonaphthol, but resinous products, and by treatment with sodium amalgam in alkaline solution it is partially reduced to naphthalene.

T. C.

**Some Naphthol-derivatives.** By C. MARCHETTI (*Gazzetta*, 9, 544—545).—*Ethyl monobrom- $\alpha$ -naphtholate*,  $C_{10}H_7Br.OEt$ , is prepared by adding a chloroform solution of bromine in theoretical proportion to a solution of ethyl  *$\alpha$ -naphthyl ether*,  $C_{10}H_7.OEt$ , also in chloroform. After evaporation, the oily product is washed with sodium carbonate

solution, cooled by a freezing mixture, and the crystalline mass thus obtained purified by pressure and recrystallisation from ether containing a little alcohol. It forms long thick prisms (m. p.  $48^{\circ}$ ) very soluble in ether and in carbon bisulphide, but insoluble in water.

*Methyl  $\alpha$ -naphtholate* or *methyl  $\alpha$ -naphthyl ether*,  $C_{10}H_7.OMe$ , may be prepared by Shaeffer's process (*Ber.*, 2, 90), except that it is necessary in order to complete the reaction to digest the mixture for 8—10 hours under a pressure of about 800 mm. of mercury. It is a colourless liquid (b. p.  $265$ — $266^{\circ}$ ) which remains liquid at  $-10^{\circ}$ . It is very soluble in ether, carbon bisulphide, and chloroform, less soluble in ethyl alcohol, sparingly in methyl alcohol, and almost insoluble in water.

*Methyl  $\beta$ -naphtholate* or *methyl  $\beta$ -naphthyl ether* crystallises in colourless plates (m. p.  $70^{\circ}$ , b. p.  $274^{\circ}$ ) having an odour of pine-apple. In solubility, it resembles the  $\alpha$ -compound; it is volatile in the vapour of water.

C. E. G.

**Nitronaphthoic Acids.** By Å. G. ECKSTRAND (*Ber.*, 12, 1393—1396).—When fuming nitric acid is added to the hot concentrated solutions of the isomeric  $\alpha$ - and  $\beta$ -naphthoic acids in glacial acetic acid, each yields two isomeric mononitro-derivatives, which may be separated by fractional crystallisation from alcohol and ether, &c.

$\alpha$ -Naphthoic acid thus gives—first, a more soluble nitro-acid, which crystallises in colourless prisms (m. p.  $195$ — $196^{\circ}$ ), and forms a sparingly soluble anhydrous calcium salt (1 in 47), and a crystalline ethyl salt (m. p.  $63^{\circ}$ ) easily soluble in alcohol and ether; also a less soluble yellowish coloured acid, in fine prisms (m. p.  $233^{\circ}$ ), soluble in alcohol, ether, glacial acetic acid, and benzene; it forms a very sparingly soluble calcium salt (1 in 160), and a crystalline ethyl salt (m. p.  $92^{\circ}$ ).

$\beta$ -Naphthoic acid gives—first, a yellowish easily soluble nitro-acid (m. p.  $220^{\circ}$ ), readily dissolved by alcohol, ether, acetic acid, and benzene, forming a slightly soluble calcium salt (1 in 388), and an ethyl salt (m. p.  $82^{\circ}$ ); also a sparingly soluble acid (m. p. about  $280^{\circ}$ ), forming a very slightly soluble calcium salt (1 in 930), and an ethyl salt (m. p.  $107^{\circ}$ ).

The alkaline salts of all four acids are easily soluble in water, their silver salts insoluble. Their constitution is as yet unknown.

Ch. B.

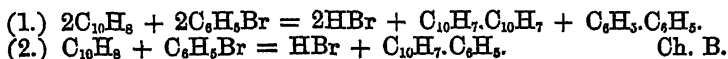
**Synthesis of Phenyl-naphthalene.** By W. SMITH (*Ber.*, 12, 1396—1398).—When a mixture of monobromonaphthalene and benzene is passed through an empty tube heated to redness, very little change takes place. But when the tube is filled with soda-lime at the same temperature, the three following reactions occur simultaneously:—

- (1.)  $2C_{10}H_7Br + 2C_6H_6 + 2NaOH = 2NaBr + 2H_2O + C_6H_5.C_6H_5 + C_{10}H_7.C_{10}H_7.$
- (2.)  $C_{10}H_7Br + C_6H_6 + NaOH = NaBr + H_2O + C_{10}H_7.C_6H_5.$
- (3.)  $C_{10}H_7Br + 2C_6H_6 + NaOH = NaBr + H_2O + C_{10}H_5.C_6H_5 + C_6H_5.C_6H_5.$



In the actual experiment, a little diphenyl and a considerable quantity of naphthalene were formed.

When a mixture of naphthalene and monobromobenzene is passed through a combustion tube, filled with pumice stone and heated to strong redness, *diphenyl*, *isodinaphthyl*, and a new hydrocarbon of lower boiling point than the dinaphthyls, are obtained mixed with the unchanged original bodies. The new hydrocarbon is soluble in hot spirit, and separates on cooling in microscopic plates, which may be sublimed in transparent scales showing blue fluorescence (m. p. 101–102°). It smells like pomegranate. It is probably *phenylnaphthalene*, produced by the second of the reactions occurring in the process:—



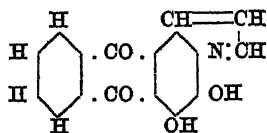
Ch. B.

**Synthesis of Anthracene.** By C. L. JACKSON and J. F. WHITE (*Ber.*, 12, 1965–1967).—A solution of orthobromobenzyl bromide in toluene when acted on by sodium yields a product which may be separated into three parts:—A, an oil which after some time becomes crystalline (m. p. about 51°), this has not yet been investigated. B, a mixture of anthracene and anthracene dihydride. C, a bituminous residue. The formation of anthracene by this reaction proves that *the two carbon atoms in anthracene are combined with both benzene-rings in the ortho-position.*

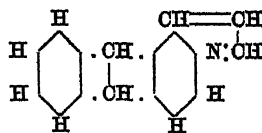
T. C.

**Constitution of Alizarin-blue.** By C. GRAEBE (*Ber.*, 12, 1416–1418).—The analyses of the salts and ethers of alizarin-blue have confirmed the author's formula for it,  $C_{17}H_8NO_4$ , and shown that its molecule contains two ketone oxygen atoms and two hydroxyl groups. The two atoms of oxygen which nitroalizarin loses in its conversion into this body by the action of glycerol (*Ber.*, 11, 1646 and 1945) are therefore those of the nitro-group.

The author considers that alizarin-blue bears to alizarin the same relation that chinoline bears to benzene, and ascribes to it and the base derived from it by heating with zinc-dust the constitution and names,



Alizarin-blue.



Anthrachinoline.

on the following grounds:—Alizarin-blue yields phthalic acid on oxidation, showing that only one benzene nucleus contains lateral chains. Moreover, the nitroalizarin of Rosenstiehl and Caro, used in preparing it, which also yields phthalic acid on oxidation, cannot be converted into purpurin like its isomeride prepared by Perkin: it must therefore contain the groups OH: OH: NO<sub>2</sub> in the positions 1: 2: 3, since according to Baeyer, the corresponding groups of purpurin have the arrangement, 1: 2: 4.

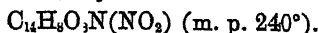
Anthrachinoline (m. p. 170°, b. p. 446°) is a tertiary base. It can

be readily oxidised into a quinone which reacts with zinc-dust and soda like anthraquinone.

The synthesis of chinoline from aniline and allyl iodide, effected by Königs (*Ber.*, 12, 453), is to a certain extent analogous to the synthesis of alizarin-blue from nitro-alizarin and glycerol. Ch. B.

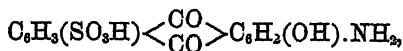
**Action of Ammonia on Anthraquinonesulphonic Acids.** By R. BOURCART (*Ber.*, 12, 1418—1420). When sodium anthraquinone-monosulphate is heated at 180° with aqueous ammonia for 48 hours, the group  $\text{HSO}_3$  is eliminated, and a body having the composition  $\text{C}_{14}\text{H}_9\text{O}_3\text{N}$  is formed. This substance is dark-red in colour, crystalline, insoluble in water, ether, and alkalis, but soluble in alcohol and benzene (m. p. 301°). By sublimation it is obtained in crystals strongly resembling those of alizarin. It has the composition of *amido-oxyanthraquinone*, but differs from known bodies of that type in being insoluble in alkalis.

Acetic anhydride converts it into a yellow triacetyl-compound (m. p. 257°) soluble in alcohol and ether; by the action of potassium nitrite and sulphuric acid, it yields a volatile nitro-derivative—



The latter when heated with zinc-dust is converted into a basic body containing oxygen (m. p. 210°), which dissolves slowly in dilute sulphuric acid; its solutions in alcohol and ether are dichroic. Its constitution is not known.

Sodium anthraquinonebisulphate (analogous to isopurpurin) when similarly treated with ammonia yields a nitrogenous body, still containing the group  $\text{HSO}_3$ ; it dissolves in ammonia with cherry-red colour, and is precipitated again by acids in pale violet flocks. The new acid probably has the constitution—



with which formula the analysis of its ammonium salt also agrees.

Ch. B.

**Products from Brown Coal-tar and some Derivatives of Chrysene.** By A. ADLER (*Ber.*, 12, 1889—1895).—The author has discovered chrysene to be the chief constituent of the residue from the rectification of the tar, prepared by distilling a variety of brown coal known as pyropissite; the following derivatives have been prepared from the chrysene so obtained.

*Dibromochrysoquinone*,  $\text{C}_{18}\text{H}_8\text{Br}_2\text{O}_2$ .—Bromine acts directly on the quinone, and by crystallisation from carbon bisulphide, the dibromo-derivative is obtained in small red leaflets, which dissolve in alcohol and benzene, but less easily in ether. It melts at 160—165°.

*Dinitrochrysoquinone*,  $\text{C}_{18}\text{H}_8(\text{NO}_2)_2\text{O}_2$ .—By dissolving chrysoquinone in nitric acid (sp. gr. 1.4) a red solution is formed, from which the dinitro-derivative is precipitated on addition of water. By crystallisation from hot acetic acid and alcohol, it is obtained in red needles (m. p. 230°) sparingly soluble in benzene and ether.

*Tribromodinitrochrysene*,  $\text{C}_{18}\text{H}_7(\text{NO}_2)_2\text{Br}_3$ .—This compound is formed

by the direct action of bromine on tetranitrochrysene; it dissolves in alcohol, from which it crystallises in yellowish-red needles, is sparingly soluble in benzene and ether. It is not decomposed by alcoholic potash.

The action of reducing agents on tetranitrochrysene yield but unsatisfactory results.

Barium chrysoquinonedisulphate,  $C_{18}H_8O_2(SO_3)_2Ba$ , is formed by treating the sulphonic acid with barium carbonate: on concentration in a vacuum it is obtained in well-formed crystals, viz., regular octahedrons. It is unstable, takes up moisture from the air, and becomes red.

P. P. B.

**Hydration of Terpenes.** By F. FLAWITZKY (*Ber.*, 12, 1406—1407).—The hydration of terpenes, shown by the author to take place under the influence of hydrochloric and sulphuric acids (*Ber.*, 12, 1022), is also effected by hydriodic and phosphoric acids, but not by oxalic and acetic acids. Using alcoholic sulphuric acid, the amount of hydrate formed is greater the more soluble the terpene is in that mixture. Thus, one part of French oil of turpentine ( $[\alpha]_D = -30^\circ$ ) mixed with one part 90 per cent. alcohol and one half part oil of vitriol (sp. gr. 1.64) and allowed to stand for ten days, is dissolved to the extent of more than one half; and on adding a little water to the solution a liquid layer separates, which solidifies when left for a few days in an open dish. By washing with water, distilling with steam and fractional distillation, an optically-inactive, pleasantly-smelling compound,  $C_{10}H_{18}O$ , is obtained, which is soluble in all proportions in alcoholic sulphuric acid of the above strength.

Sulphuric acid also acts on certain terpenes ( $[\alpha]_D = -36^\circ$  and  $[\alpha]_D = +24^\circ$ ) from Russian oil of turpentine, but very slightly on oil of lemon ( $[\alpha]_D = +55^\circ$ ). Alcoholic nitric acid also dissolves oil of turpentine.

Ch. B.

**Abietic Acid.** By O. EMMERLING (*Ber.*, 12, 1441—1446).—The most important work with reference to this acid is that of Maly (*Annalen*, 132, 249), who ascertained its composition,  $C_{20}H_{30}O_6$ , and considered that it is produced by hydration from colophonium,  $C_{20}H_{30}O_4$ . Maly prepared several of its compounds, including the ethyl salt,  $C_{20}H_{32}(C_2H_5)_2O_6 + \frac{1}{2}H_2O$ , and the glycerol salt, *abietin*. By the action of sodium amalgam, he converted it into *hydroabietic acid*,  $C_{20}H_{30}O_5$ ; and by fusion with potash obtained, besides some propionic acid, a potash salt which was soluble in water, but insoluble in potash solution, and was not a protocathecuete. By the action of phosphoric chloride, he obtained various hydrocarbons. Amongst later investigators (Flückeger, Schreder and others) Ciamician (*Ber.*, 11, 269) heated it with zinc-dust and obtained *toluene*, *metethylmethylbenzene*, *methylnaphthalene* and *methylanthracene*.

Abietic acid is best obtained pure by digesting colophonium with 70 per cent. alcohol for a couple of days, washing the undissolved portion with weak spirit, and dissolving it in the smallest quantity of glacial acetic acid. From this solution, the acid gradually separates in crusts. By adding a little water to its solution in hot alcohol and stirring, the

acid may be obtained in crystalline scales (m. p.  $139^{\circ}$ ; Lievert, *Jahresbericht*, 1859, 508, gives  $150^{\circ}$ ; Maly  $165^{\circ}$ , and Flückeger  $135^{\circ}$ ). By slow evaporation of its alcoholic solution, it is obtained in equilateral triangular crystals.

Abietic acid probably contains hydroxyl-groups. When heated with acetic chloride or anhydride it yields a neutral oil which could not be purified, and was therefore not analysed. Since, however, it gives up acetic acid to boiling potash, it is evidently an acetyl compound. By adding bromine to a solution of abietic acid in carbon bisulphide a bromine derivative is formed, probably  $C_{44}H_{82}Br_2O_8$ , which separates from alcohol as a red powder (m. p.  $134^{\circ}$ ).

When abietic acid is distilled with zinc chloride, a heavy oil is produced, which has the properties of Anderson's resin-oil (*Jahresbericht*, 1869, 787). A portion of this liquid, boiling between  $70^{\circ}$  and  $250^{\circ}$ , may be separated by water vapour; the part which comes over between  $80^{\circ}$  and  $100^{\circ}$  contains *heptylene*, since on treatment with hydriodic acid it yields *heptyl iodide*.

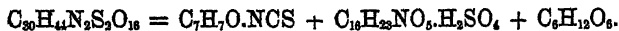
Strong hydriodic and hydrochloric acids at  $145^{\circ}$  appear to dehydrate abietic acid, reproducing colophonium. Fusing potash does not attack it. By oxidation with permanganate, carbonic, acetic and formic acids are produced. When it is boiled with chromic mixture, acetic acid is formed in large quantity; and after this has been removed by distillation, ether extracts from the liquid a little *trimellitic acid*,  $C_6H_2(COOH)_3$ , which was converted into barium salt and analysed. The acid separated from this salt is crystalline, and by sublimation yields trimellitic anhydride (m. p.  $158^{\circ}$ ). Ch. B.

**The Glucoside from White Mustard-seed.** By H. WILL and A. LAUBENHEIMER (*Annalen*, 199, 150—164).—*Sinalbin*,  $C_{30}H_{44}N_2S_2O_{16}$ , is prepared by extracting with warm alcohol white mustard seed (*Sinapis alba*) from which the oil has been removed by pressure and by treatment with carbon bisulphide. The crystals which are deposited are washed with carbon bisulphide and dissolved in a small quantity of hot water: the solution is then boiled with animal charcoal, filtered, and mixed with strong alcohol, and the precipitate which is formed is recrystallised from alcohol, when pale-yellow needle-shaped crystals of sinalbin are obtained. The mother-liquor from the crude sinalbin contains sinapin thiocyanate. Sinalbin is insoluble in ether and carbon bisulphide, sparingly soluble in cold absolute alcohol, but freely soluble in water. The aqueous solution has a neutral reaction; when brought in contact with a trace of an alkali, it acquires an intense yellow colour which is turned red by nitric acid. Silver nitrate throws down a white precipitate which consists of the silver compounds of sinapin and of sinalbin thiocarbimide; the filtrate, which has a strongly acid reaction, contains sinapin (which may be precipitated by mercuric chloride) and grape-sugar. When the precipitate is decomposed by sulphuretted hydrogen, *sinapin sulphate*,  $C_{16}H_{24}NO_4.HSO_4$ , and the *cyanide*,  $C_6H_4(OH)CH_2CN$ , pass into solution; the latter can be extracted with ether. After recrystallisation, from benzene, the cyanide forms colourless plates (m. p.  $69^{\circ}$ ) soluble in ether, alcohol, warm benzene, and warm water. On boiling with potash, ammonia is evolved

and *orthohydroxyphenylacetic acid*,  $C_8H_4(OH)CH_2.COOH$ , is produced. The acid crystallises in colourless prisms (m. p.  $144.5^\circ$ ), soluble in alcohol, ether, and hot water, and bears some resemblance to Salkowski's parahydroxyphenylacetic acid (*Ber.*, 12, 1438). The *calcium salt*,  $(C_8H_4O_3)_2Ca + 4H_2O$ , forms glistening prisms, sparingly soluble in cold water: the *barium salt*,  $(C_8H_4O_3)_2Ba + H_2O$ , triclinic prisms, slightly soluble in cold water. The *silver salt*,  $C_8H_4O_3Ag$ , is almost insoluble in water, and is decomposed by heat.

On the addition of mercuric chloride to a warm aqueous solution of sinalbin, a precipitate is produced which contains, in addition to compounds of mercury with sinapin sulphate and the cyanide,  $C_7H_7OCN$ , a double chloride, viz.,  $C_{18}H_{23}NO_5.HgCl_2$ .

If ground white mustard-seed is treated with water and filtered, an acid liquid is obtained which contains myrosin, sugar, sinapin thiocyanate, and sulphate. The myrosin may be precipitated from this solution by alcohol. An aqueous solution of sinalbin is decomposed by myrosin, thus:—



Sinalbin. Sinalbin thiocarbimide. Sinapin sulphate. Sugar.

The pungent principle in the mustard-seed is contained in the albuminous precipitate, which separates out on the addition of the myrosin; by extraction with alcohol and ether it can be obtained in the impure state as a yellow oil insoluble in water. W. C. W.

**Chlorophyll.** By A. GAUTIER (*Compt. rend.*, 89, 861—866).—The author succeeded in obtaining pure crystallised chlorophyll in the year 1877, by the following process. The green leaves of spinach and cresses were bruised in a mortar, with addition of sodium carbonate, so as to neutralise the acidity of the juice, and then pressed. The solid residue was suspended in alcohol of  $55^\circ$ , and again pressed, and the process repeated with alcohol of  $83^\circ$ . Chlorophyll, wax, fats, and pigments dissolve. The liquid is filtered, and then shaken with pure animal charcoal. The green colouring matter is absorbed after several days; the charcoal is washed with alcohol of  $65^\circ$ , which removes a yellow crystallisable substance. It is then washed with dry ether, or light petroleum, when the chlorophyll dissolves, and is deposited in dark-green crystals by slow evaporation.

It forms needles of as much as half a centimeter long, of soft consistence; on keeping it turns yellowish- or greenish-brown. Some of the smaller crystals transmit green light, and some lilac. The crystalline form appears to be an oblique rhomboidal prism, the rhombohedral angle being about  $45^\circ$ . As thus obtained, chlorophyll presents striking analogy to bilirubin; it is soluble in the same solvents; it is removed from its solutions by animal charcoal, and may be again recovered by treatment with ether or petroleum; it forms salts with bases; it is easily oxidised in presence of light; it undergoes numerous changes, accompanied by alteration of colour; and it combines directly with nascent hydrogen. When digested with hydrochloric acid, it splits up into *phylloxanthin*, a brown substance, crystallising from ether or hot alcohol, and Frémy's *phyllocyanic acid*, an olive-green substance,

soluble in alcohol and ether, and forming salts with bases. Chlorophyll thus prepared is absolutely free from iron. The "chlorophyllane" discovered by Hoppe-Seyler (an account of which is published in *Ber.*, 12, 1555), closely agrees in its properties with the substance separated by the author. The analyses of the two bodies are also fairly concordant. Hoppe-Seyler's chlorophyllane contains C = 73.4; H = 9.7; N = 5.62; P = 1.37; Mg = 0.34; O = 9.57; and the author's analysis of chlorophyll which had turned yellow from exposure to light is C = 73.97; H = 9.80; N = 4.15; ash = 1.75; O = 10.33. The author concludes by remarking that his discovery was two years prior to that of Hoppe-Seyler, and he has been induced to publish in consequence of the latter's recent paper.

W. R.

**Colouring-matter of Anguria and Colocyntn.** By A. and G. DE NEGRI (*Gazzetta*, 9, 506—507).—In the fruit of *Ocucumis anguria*, a very unstable red colouring-matter exists, which the authors have named *rubidine*. It may easily be obtained by exhausting the fruit with ether, evaporating, and treating the residue with absolute alcohol; this dissolves a yellow colouring-matter, and leaves the rubidine in the crystalline state. It is insoluble in water, but easily soluble in benzene, chloroform, or carbon bisulphide; the solutions giving a characteristic spectrum, with two absorption-bands in the green, and another less distinct in the blue. It crystallises in beautiful red needles with yellowish-green metallic reflex; it is not altered by the action of ammonia, but becomes blue when treated with concentrated sulphuric or nitric acid. It is not volatile, but carbonises when strongly heated.

It is probable that rubidine exists in other plants; in fact the authors have extracted a red crystalline substance from colocyntn, very closely resembling rubidine in its properties, and apparently identical with it.

C. E. G.

**Lapachic Acid.** By E. PATERNO (Preliminary Notice) (*Gazzetta*, 9, 505—506).—This acid is obtained from the "lapacho" wood, furnished by a tree of the order *Bigoniaceæ*, indigenous to the Argentine Republic and other parts of South America. The formula of the acid is  $C_{15}H_{14}O_8$ , and that of its silver salt,  $C_{15}H_{13}AgO_8$ ; treated with acetic chloride or anhydride it yields a crystalline acetate,  $C_{15}H_{13}Ac_2O_8$ , whilst with bromine it gives the compound  $C_{15}H_{13}BrO_8$ , crystallising in orange-coloured plates. It is almost entirely converted into phthalic acid by the action of nitric acid, and yields naphthalene and isobutylene when distilled with zinc turnings. The acid appears to be identical with Stein's *groenhartin* and with Arnoudon's *tauguic acid*.

C. E. G.

**Compounds from Animal Tar.** By H. WEIDEL (*Ber.*, 12, 1989—1912).—Since the oxidation-products (nicotinic acid, cinchomeronic acid, oxycinchomeronic acid, berberonic acid) of certain alkaloïds gave chiefly pyridine by the dry distillation of their lime-salts, whilst others (cinchonine and chinolic acid) gave chinoline, a more minute examination of the bases from animal tar than had hitherto been made appeared very desirable. Animal tar begins to boil at about 80°, when an oily distillate mixed with water passes over

accompanied by a considerable evolution of ammonia. The temperature then rises gradually to  $250^{\circ}$ , beyond which the distillation cannot be carried conveniently on account of the rapid sublimation of ammonium cyanide, ammonium carbonate, &c. The bases (picoline, pyridine, &c.) were separated and isolated from the above distillate by a process described in the original paper. 1,400 kilos. of tar gave 18.5 kilos. of the dry bases, boiling between  $95^{\circ}$  and  $250^{\circ}$ .

The picoline obtained boiled at  $133\text{--}139^{\circ}$ . Several analyses and a vapour-density determination of the lowest and highest boiling portions gave numbers corresponding with the formula,  $C_6H_7N$ , but different oxidation-products were obtained from each, showing that they were not identical. Devar (*Zeits. Chem.*, 1871, 116) obtained pyridinedicarboxylic acid,  $C_7H_5NO_4$ , by the oxidation of picoline with potassium permanganate; the author, however, using exactly the same process, did not obtain this acid, but two other acids having the composition  $C_6H_5NO_4$ ; he afterwards succeeded in obtaining Devar's pyridinedicarboxylic acid, but only from those portions of the distillate from the tar having the composition of lutidine. The two acids obtained above by the oxidation of picoline were separated by means of the difference in the solubility of their copper salts which were then decomposed by sulphuretted hydrogen.

*Picolinic Acid*,  $C_6H_5NO_2$ .—This is the acid obtained from the less soluble copper salt. It crystallises in prismatic needles (m. p.  $135^{\circ}$ ) which are easily soluble in alcohol and in water, but almost insoluble in ether, benzene, chloroform, and carbon bisulphide. It is odourless, and has an acid taste, afterwards bitter. On adding a copper salt to a not too dilute solution of this acid or its salts, a precipitate of brilliant violet-blue needles or plates is produced: this characteristic action may be used for the identification of the acid. It is monobasic; the potassium, sodium, ammonium, calcium [ $(C_6H_4NO_2)_2.Ca + 1\frac{1}{2}H_2O$ ], barium [ $(C_6H_4NO_2)_2.Ba + H_2O$ ], magnesium [ $(C_6H_4NO_2)_2.Mg + 2H_2O$ ], cadmium, and copper salts, were prepared and described. The *hydrochloride*,  $C_6H_5NO_2.HCl$ , crystallises in large colourless crystals, and gives a platinumchloride,  $(C_6H_5NO_2.HCl)_2.PtCl_4 + H_2O$ , of sp. gr. 2.0672 at  $22^{\circ}$ .

Picolinic acid may be considered as pyridinecarboxylic acid,  $C_5H_5N.CO_2H$ , being obtained by the oxidation of picoline or methyl pyridine,  $C_5H_5N.CH_3$ . This view is further confirmed by the fact that pyridine, together with a small quantity of dipyridine, is formed by the dry distillation of its calcium salt with quick-lime, or on heating the acid with alcoholic potash in sealed tubes at  $240^{\circ}$ . The sodium salt of picolinic acid by reduction with sodium-amalgam, gives a new acid, *oxysorbic acid*,  $C_6H_5O_3$ , whilst ammonia is evolved. Oxysorbic acid crystallises in colourless needles (m. p. about  $85^{\circ}$ ) which are exceedingly deliquescent and very soluble in water, but almost insoluble in hot or cold alcohol. It reduces Trommer's copper solution. The calcium, barium, and cadmium salts were prepared; they are all amorphous.

*Nicotinic Acid*,  $C_6H_5NO_2$ .—This acid, obtained together with picolinic acid by the oxidation of picoline, crystallises in needles (m. p.  $228^{\circ}$ ), and is identical with the acid previously obtained by the author

(*Annalen*, 165, 328), and also by Laiblin (*Ber.*, 10, 2136). Nicotinic acid, like picolinic acid, by the dry distillation of its calcium salt, yields pyridine, whilst reduction with sodium-amalgam converts it into oxysorbinic acid. A table is given showing the more important differences between picolinic and nicotinic acids.

The formation of two distinct acids from picoline shows that the latter is a mixture of two isomeric compounds, which cannot be separated by fractional distillation. This can, however, be attained by making use of the different solubilities of their platinochlorides. The  $\alpha$ -picoline compound being less soluble than that of  $\beta$ -picoline.

$\alpha$ -Picoline (b. p.  $134^\circ$ , uncorr.) is optically inactive, and gives on oxidation *only* picolinic acid. The platinochloride, according to the condition of its formula  $(C_6H_7N.HCl)_2 + PtCl_4 + H_2O$ , can be obtained either anhydrous or with water of crystallisation.

$\beta$ -Picoline (b. p.  $140^\circ$ ) is slightly laevorotatory, and on oxidation gives *only* nicotinic acid; it is less soluble in water than  $\alpha$ -picoline. The picoline which Baeyer obtained synthetically by the dry distillation of the ammonia compound of acrolein (*Annalen*, 155, 281), is not identical with either  $\alpha$ - or  $\beta$ -picoline, and therefore forms the third of Körner's three possible picolines. T. C.

**Some Derivatives of Cinchonine.** By A. WISCHNEGRADSKY (*Ber.*, 12, 1480—1482).—Butlerow and Wischnegradsky have shown (*Ber.*, 11, 1253) that cinchonine, under certain as yet undefined conditions, is decomposed by fusing potash into chinoline and a base which they have further resolved into a fatty acid and ethyl-pyridene. The latter base is a pleasantly-smelling liquid (b. p.  $166^\circ$ ), soluble in water with difficulty. It combines with platinum and mercuric chlorides, and by oxidation with a 30 per cent. chromic acid solution in presence of sulphuric acid, yields Laiblin's *monocarbopyridenic* (nicotinic) acid,  $C_7H_7N + 3O_2 = C_6H_5O_2N + CO_2 + 2H_2O$ . It is isomeric, or identical with Anderson's *lutidine*.

With regard to chinoline, the author finds that by oxidation with chromic and sulphuric acids, it yields Ramsay and Dobbie's *dicarbopyridenic acid* (this Journal, 35, 189), obtained by oxidation of cinchonine. This reaction harmonises with Körner's view of its constitution, confirmed by Baeyer and König's synthesis, viz., that it is naphthalene in which the group CH has been replaced by N. By reduction with zinc and hydrochloric acid, chinoline yields a resinous base, which forms uncrystallisable salts, and a base having nearly the same boiling point as itself, and forming a crystalline compound with hydrochloric acid.

These experiments lead to the conclusion that cinchonine contains a *methylchinoline* and an *ethylpyridine* nucleus. By the addition of hydrogen, the double union of carbon and nitrogen in the two nuclei may be supposed to be loosened; and from the hypothetical *secondary* bases thus formed, cinchonine may be constituted by the intervention of the acid radicle  $CH_3.CH.CO$  or  $CH_3.CH_2.CO$ , thus:—



By oxidation, these hydrogenated bases are reconverted into the



tertiary bases (or their derivatives), pyridine and chinoline. Fusing potash acts on cinchonine in two ways, partly by oxidising it to cinchonic acid, and partly by decomposing it, with reduction, into methylchinoline. The potash further decomposes the cinchonic acid with formation of chinoline. As a fact, chinoline prepared from cinchonine always contains methylchinoline or lutidine (Williams and Wischnegradsky).

If the constitution of cinchonine given above is correct, it should be obtained synthetically by acting with dihydrolepidine and dihydroethylpyridine on the chloranhydride of one of the chloropropionic acids. Ch. B.

**Homocinchonidine.** By Z. H. SKRAUP (*Annalen*, 199, 359—368).—Cinchonidine and Hesse's homocinchonidine (*Ber.*, 10, 2156) are identical in crystalline form and melting point, and they have the same composition,  $C_{19}H_{22}N_2O$ , and rotatory power. The determinations of the solubility of the alkaloids in water, ether, and alcohol, yield slightly varying results. Since the salts of homocinchonidine and cinchonidine resemble each other in every respect, the author concludes that the two bases are identical. W. C. W.

**Quinamine.** By O. HESSE (*Annalen*, 199, 333—337).—Analyses of the free base and of the hydriodide and platinochloride show that quinamine has the composition  $C_{18}H_{24}N_2O_2$ .

The alkaloid is dextrogyrate; the rotatory power of its solutions is seen from the following numbers,  $p = 2$  and  $t\ 15^\circ$ :—

| Solvent.                 | $\alpha_D$ . |          |
|--------------------------|--------------|----------|
| 97 per cent. alcohol.... | + 104.50°    |          |
| Chloroform .....         | + 93.50      |          |
| Water + 1 mol. HCl..     | + 116.03     |          |
| Water + 3 mols. HCl..    | + 117.18     | W. C. W. |

**A New Organic Acid, Lithobilic Acid.** By G. ROSTER (*Gazzetta*, 9, 462—471).—In the author's paper on lithofellic acid (this vol., p. 181), he mentioned that in recrystallising the crude precipitated barium lithofellate, a substance remained undissolved, apparently the barium salt of a new acid; this is of a resinoid nature, and after being thoroughly washed with boiling water, in which it is almost insoluble, is obtained as a yellowish amorphous semitransparent mass. It melts at  $109^\circ$ , and on treatment with acids, it is decomposed with liberation of the new acid. Although this barium salt is usually amorphous, it was on one occasion obtained in a crystalline state, on allowing a hot filtered solution of crude barium lithofellate to evaporate spontaneously. The crystals, which were exceedingly minute, were of rhombohedral habit, but owing to their smallness, but few measurements could be taken. Two analyses of the barium salt were made, the results agreeing with the formula  $C_{20}H_{27}O_6.H$ .

*Lithobilic acid* was prepared by decomposing the barium salt with dilute hydrochloric acid, and after carefully washing with warm water, crystallising it from alcohol. The acid forms tufts of long needles,

of a slightly yellowish tinge (m. p. 199°). It is insoluble in water, moderately soluble in ether, and readily in alcohol even in the cold. Heated with concentrated hydrochloric acid, it is decomposed and dissolved with a very beautiful violet-rose coloration. Its alcoholic solution is dextrorotatory; the specific rotatory power for D being greater than that of lithofellic acid.

In conclusion, the author points out the difference in properties between lithofellic and lithobilic acids, such as the difference in the solubility of the barium salts, the difference in melting points, &c. The new acid would seem to belong to the group of biliary acids, as it gives Pettenkofer's reaction, and, when burned, emits the peculiar aromatic odour characteristic of the biliary acids. C. E. G.

**Constitution of Stag's Horn.** By A. BLENNARD (*Compt. rend.*, 89, 953—954).—Purified stag's horn gave the following numbers on analysis:—

- I. C, 45·03; H, 7·3; N, 16·01; Ash, 2·4.  
 II. C, 44·90; H, 7·0; N, 15·5; Ash, 2·3.

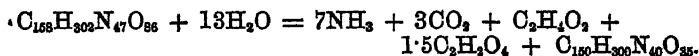
On digestion with baryta in an autoclave at 150° for 48 hours, it gave—



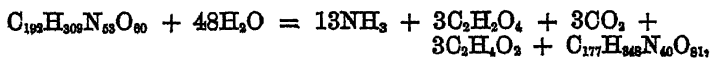
Analysis of the residue, which amounted to 95 per cent. of the purified horn, gave—

- I. C, 44·8; H, 7·5; N, 13·9; Ash, 0·37.  
 II. C, 44·5; H, 7·45; N, 13·8.

These results correspond with the equation—



Comparing this equation with that deduced by Schützenberger from similar experiments with albumin, viz.,



the following inferences are drawn:—that stag's horn is a lower homologue of coagulated egg albumin, and is more hydrated; and each molecule of carbonic and oxalic acids formed corresponds approximately to two molecules of ammonia; whilst oxalic and acetic acids are evolved in nearly equivalent amounts. W. R.

## Physiological Chemistry.

**Gaseous Nitrogen, a Product of the Decomposition of Albuminoids in the Body.** By J. SEEGEN and J. NOWAK (*Pflüger's Archiv. f. Phys.*, 19, 347—415). — The authors criticise, at great length, the work of Viot and Pettenkofer, especially Viot's statement that the whole of the nitrogen resulting from the decomposition of albuminoids within the body is to be found in the urine and excrement. They point out possible sources of error in the experimental methods adopted by Viot, and in the respiration apparatus of Pettenkofer. An apparatus is minutely described, composed entirely of glass and metal, all joints being made tight by means of mercury, and by the use of which they claim to have established the facts, that a por-

| Duration of experiment in hours. | Animal employed. | Weight in grams of animal. | Grams of gaseous nitrogen expired per hour per kilo. weight of animal. | Total grams of nitrogen expired. |
|----------------------------------|------------------|----------------------------|--|----------------------------------|
| 15                               | Rabbit           | 2010                       | 0·0058   | 0·176                            |
| 36                               | Do.              | 2010                       | 0·0064   | 0·465                            |
| 29                               | Cock             | 1950                       | 0·009  | 0·525                            |
| 23                               | Do.              | 1800                       | 0·007  | 0·288                            |
| 16                               | 4 Pigeons        | 1500                       | 0·0077   | 0·187                            |
| 55                               | Do.              | 1500                       | 0·007  | 0·583                            |
| 72                               | 2 Fowls          | 2011                       | 0·007  | 1·004                            |
| 12                               | Dog              | 4100                       | 0·008  | 0·896                            |
| 17                               | Do.              | 4100                       | 0·008  | 0·551                            |
| 24                               | Do.              | 4100                       | 0·0081   | 0·804                            |
| 60                               | Do.              | 4100                       | 0·0081   | 1·097                            |
| 40                               | 4 Rabbits        | 7900                       | 0·005  | 1·595                            |
| 18                               | Do.              | 7900                       | 0·0043   | 0·628                            |
| 25                               | Fowl             | 1520                       | 0·009  | 0·351                            |
| 16                               | 5 Fowls          | 5500                       | 0·0089   | 0·779                            |
| 62                               | Dog              | 4200                       | 0·009  | 2·384                            |
| 60                               | 4 Fowls          | 4400                       | 0·0084   | 2·200                            |
| 72                               | 3 Do.            | 3500                       | 0·0087   | 2·197                            |
| 46                               | 8 Pigeons        | 3600                       | 0·009  | 1·532                            |
| 70                               | Dog              | 3500                       | 0·0085   | 2·085                            |
| 60                               | Do.              | 3500                       | 0·0081   | 1·726                            |
| 56                               | Rabbit           | 2050                       | 0·004  | 0·435                            |
| 60                               | Fowl             | 1000                       | 0·008  | 0·515                            |
| 108                              | Do.              | 1000                       | 0·0083   | 1·995                            |
| 48                               | Fowl             | 1350                       | 0·008  | 0·527                            |
| 43                               | 3 Pigeons        | 1300                       | 0·0077   | 0·432                            |
| 96                               | Rabbit           | 2200                       | 0·0053   | 1·130                            |
| 110                              | Do.              | 2800                       | 0·006  | 1·896                            |
| 32                               | Dog              | 6500                       | 0·0076   | 1·585                            |
| 68                               | Do.              | 6500                       | 0·0063   | 2·868                            |
| 98                               | 5 Rabbits        | 10400                      | 0·0047   | 4·767                            |
| 70                               | 5 Fowls          | 6000                       | 0·0078   | 3·800                            |

tion of the nitrogen which results from the decomposition of albuminoids in the bodies of animals passes out of the system in the gaseous form; and that the amount of nitrogen thus expired increases, within narrow limits, in direct proportion to the duration of the experiment and the weight of the animal employed.

As the point discussed is of importance, a table is given in which the actual results obtained are grouped together.

The cubic contents of the apparatus were determined, and thus the total nitrogen, in grams, could be found from analysis of the air passing through the apparatus. M. M. P. M.

**Chemical Composition of Milk.** By L. SCHISCHKOFF (*Der.*, 12, 1490—1492).—Adopting the view that milk is an emulsion of fat, the author has made attempts to emulsify different fats. A weak solution of potassium or sodium carbonate ( $\frac{1}{4}$ th per cent.) will only emulsify those fats which contain free fatty acid, even though in minute quantity. The richer the fat is in solid constituents, the more easily is it emulsified; fats poorer in solids require a larger proportion of free fatty acids. A fat must, however, be liquefied before it can form an emulsion; the ease with which it does so depends therefore not on its firmness at ordinary temperatures, but on the superior attraction exerted by the emulsifying liquid on a solid over a liquid fat. An alkaline solution emulsifies a fat, when its smallest particles exert a sufficient attraction on any one constituent of the fat, even though absolutely indifferent to the remainder. Thus, oil of turpentine, mineral oil, &c., may be easily emulsified if mixed with a little stearic acid. A fat which cannot be emulsified in an alkaline liquid will be so easily when a different fat has been previously emulsified in the same liquid. The fat extracted from cow's milk by a mixture of alcohol and ether contains a certain quantity of fatty acids, and hence easily forms an emulsion. Melted butter, which contains relatively little free acid and solid fat, is emulsified with much less ease. The liquid part of butter is almost incapable of forming an emulsion, but does so easily when mixed with solid fat and a little free fatty acid. Conversely, cow fat completely loses its power of forming an emulsion after washing with a solution of an alkaline carbonate. It is singular that alkaline carbonates are chiefly attracted by, and combine with, the solid fats of butter. The author has not yet accurately determined what acids render milk fat emulsifiable: but amongst them are myristic, capric, caproic, and perhaps butyric acids, as may be concluded from some of the properties of their salts, and from their melting points. An emulsion may be pronounced good when it is brilliantly white, adheres strongly to glass, and on standing slowly separates a layer considerably thicker than the original fat. Under the microscope it appears to be formed of small globules, nearly uniform in size.

The formation of an emulsion thus evidently depends on the division of the fat into minute globules, and the fixation of the emulsifying liquid on their surface by the molecular attraction exerted upon it by one of their constituents. The greater this attraction, the smaller will be the globules, but the more unstable the emulsion. Shaking favours the

division of the globules, and therefore the decomposition of the emulsion. The most permanent emulsions are furnished by fats containing fatty acids which do not easily combine with alkalis, since the alkaline salts of fatty acids attract fats but feebly. By prolonged shaking an emulsion is completely decomposed into fat and soap, which do not further act on each other.

Intermediate products are obtained by partial decomposition. An emulsion is decomposed on keeping, by cooling, and by dilution with water, alcohol, or ether, and by such operations as hasten saponification, viz., heating, addition of strong alkali, &c. Albuminous matters added in excess decompose it very easily, forming soap-like compounds containing fatty acids, fat, albumin, and alkalis, or even salts. These compounds have little attraction for the excess of fat, wherefore the latter separates. The fat contained in these compounds cannot be extracted by alcohol or ether alone, but may be so by a mixture of the two. Albuminous matters decompose emulsions less easily in presence of calcium salts, since a mixture of albumin with these salts, especially the phosphates, strongly attracts fats.

That milk is an emulsion of fat in a liquid containing albumin, salts, and sugar, the author has proved by preparing a similar artificial emulsion closely resembling it. The changes taking place in milk when kept depend on the formation of various new emulsions. The composition of the cream is different at different periods of its formation. The first portions give the best butter, and consist of fat, alkaline phosphates, and albumin, forming a compound insoluble in water and weak acids; the later portions are richer in albumin and lime salts. These latter emulsions consist of smaller globules, contain free fatty acid, and yield a much coarser butter. About the time of their separation the milk begins to turn sour, and consequently all the substances which are insoluble in weak acids, and have a sufficiently low specific gravity, pass into the cream. If the souring of the milk be prevented, very little cream will be formed. Butter consists of fat, and an emulsion containing lime, insoluble in water.

Finally, the author has discovered in whey an albuminoid which is different from common albumin and from casein. Synthetic experiments have shown that casein without albumin may form milk, but not cream. These two albuminoids together go to form milk and cream; but the latter is only obtained in its natural form, when the third modification is present.

Ch. B.

**Combinations of Phosphoric Acid in the Nervous Substance.** By L. JOLLY (*Compt. rend.*, 89, 756—758).—Phosphoric acid occurs in the nervous substance as glycer- or oleo-phosphoric acid, and on ignition of the brain substance a residue, consisting of phosphoric acid and alkaline phosphates, and carbonates is left. The results obtained by the ignition of 100 grams of the brain substance of the ox and calf, and the spinal marrow of the ox are as follows:—

|                         | Brain of calf. | Brain of ox. | Spinal marrow<br>of ox. |
|-------------------------|----------------|--------------|-------------------------|
| Free phosphoric acid .. | —              | 0·095        | 0·874                   |
| Potassium phosphate ..  | 4·774          | 1·851        | 2·310                   |
| Sodium „ ..             | 0·104          | 0·206        | 0·105                   |
| Magnesium „ ..          | 0·054          | 0·178        | 0·076                   |
| Iron „ ..               | 0·088          | 0·309        | 0·154                   |
|                         | <hr/> 5·020    | <hr/> 2·639  | <hr/> 3·519             |

The phosphoric acid in combination with alkalis is calculated as potassium phosphate.

These results show that in the young animal, the brain is very rich in phosphates, whilst in the full grown animal, the spinal cord contains more phosphoric acid, and that after the alkaline phosphates, phosphate of iron is most abundant.

L. T. O'S.

**Distribution of Phosphates in the Muscles and Tendons.** By L. JOLLY (*Compt. rend.*, 89, 958—959).—Although the total amount of phosphates in muscle has been determined, analyses are wanting in which the separate phosphates have been estimated. The author has analysed the muscle of the calf, and of thin and fat oxen, with the following results:—

100 grams of dried muscular tissue contain:—

|   | Calf.       | Thin ox.    | Fat ox.     |
|---|-------------|-------------|-------------|
| Alkaline-phosphates .....                       | 0·971       | 0·021       | 1·201       |
| Calcium „ .....                                 | 0·099       | 0·060       | 0·350       |
| Magnesium „ .....                               | 0·135       | 0·073       | 0·430       |
| Iron „ .....                                    | 0·042       | 0·040       | 0·065       |
| Iron oxide, uncombined with<br>phosphorus ..... | —           | —           | —           |
|   | <hr/> 1·247 | <hr/> 0·394 | <hr/> 2·046 |

The ash of tendons was also analysed—

|                           | Calf.       | Ox.         |
|---------------------------|-------------|-------------|
| Alkaline phosphates ..... | 0·480       | 0·185       |
| Calcium „ .....           | 0·048       | 0·396       |
| Magnesium „ .....         | 0·060       | 0·136       |
| Iron „ .....              | 0·110       | 0·061       |
|                           | <hr/> 0·698 | <hr/> 0·776 |

W. R.

**Distribution of Copper in the Animal Kingdom.** By M. GIUNTI (*Gazzetta*, 9, 546—555).—After noticing the statements of various chemists as to the existence of appreciable quantities of copper in various parts of the human system, Cloez' researches on the blood of the goat, and Church's on the red pigment in the feathers of certain of the Mnsophagidæ, the author describes his own experiments, which he was induced to undertake on discovering copper in some bat's guano from a cave at Santagata d' Esaro; various samples of

this were found to contain from 0.348 to 0.403 per cent. of cupric oxide,  $\text{CuO}$ . The next step was to examine the bats whose excrements had formed the guano; several of these were incinerated and the copper estimated in the ash: it was found to be 0.039 per cent., equivalent to 0.0014 on the original weight of the bats. It is worthy of note that the proportion of copper found in these animals is much less than in the guano, which confirms the observations of Paul and Kingzett, that when copper is exhibited internally, the greater portion passes out with the excrements. Lastly, the food of these insectivorous animals was examined. Various species of insects (more than 20 in number) belonging to the natural orders Hymenopteræ, Coleopteræ, and Lepidopteræ, were tested for copper, and it was found in every case.

Other animals examined were the hedgehog, of which the ash yielded 0.02 per cent.  $\text{CuO}$ , and a species of lizard (*Podercis muralis*). In the latter the amount of copper was very variable, but the mean of 18 individuals gave 0.0565 per cent. on the ash. Two species of Coleopteræ were examined, *Anomala vitis* giving 0.095, and *Blatta orientalis* 0.826 per cent. on the ash. The very large quantity of copper in the last named insect is accounted for by their coming in contact with copper vessels in their excursions about the house in search of food. Two Myriapods were examined (*Julus terrestris* and *Armillidium vulgare*), the ash of the former containing 0.221, and that of the latter 0.197 per cent.  $\text{Cu}$ . A mollusc (*Helix pisana*) gave 0.089. The results already obtained are sufficient to show that copper is very widely distributed in the animal kingdom.

C. E. G.

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## Chemistry of Vegetable Physiology and Agriculture.

**Alcoholic Fermentation.** By D. COCHIN (*Compt. rend.*, 89, 786—787).—To prove the existence of a soluble ferment, yeast-water was prepared from beer-yeast, according to Pasteur's method, by boiling it with water in the proportion of 100 grams per litre, and filtering at once. The filtrate was mixed with beer-wort, at a temperature of 25 to 30°, no fermentation set in, but on sowing some of the residue in beer-wort, fermentation took place with great rapidity. This appears to contradict Berthelot's statement (*ibid.*, 83, 9) that a soluble ferment does exist.

L. T. O'S.

**Remarks on Cochin's Note relating to Alcoholic Fermentation.** By BERTHELOT (*Compt. rend.*, 89, 806—808).—Cochin has attempted to continue Claude Bernard's work by some observations on the actual process of fermentation of sugar with beer-yeast, and failed in separating a soluble ferment from an extract of beer-yeast, in which the yeast itself was growing. Now a liquid in which yeast is actually growing does not cause alcoholic fermentation, and if a soluble ferment exists at all, it must be sought for under conditions analogous

to those in which digestive ferments are formed, viz., under the influence of the food which the ferment is intended to digest. W. R.

**Alcoholic Fermentation: Reply to Berthelot.** By D. COCHIN (*Compt. rend.*, 89, 992—994).—The author replies to Berthelot's criticism, that yeast actually growing does not provoke fermentation, by stating that the ferment he used was stable, contained no organisms in the state of growth, and although capable of inverting sugar, did not induce alcoholic fermentation. W. R.

**Vital Power of Schizomycetes in Absence of Oxygen.** By J. W. GUNNING (*J. pr. Chem.*, 20, 434—443).—The author has previously published an account of his researches (this Journal, 1878, Abst., 267, 907), from which he draws the conclusions that substances capable of putrefaction when enclosed in vessels from which nearly all oxygen has been removed act for only a short time; and when oxygen has been completely removed by means of a solution of grape-sugar in caustic soda mixed with indigo, no putrefaction occurs, and the organisms which produce putrefaction are killed. The present paper is a reply to Nencki's objections, who stated that Gunning's experiments were inaccurate.

Gunning has shown that the apparatus employed to produce what Nencki termed "space freed from oxygen" is insufficient for that purpose, and contains enough oxygen to colour ferrous ferrocyanide deep blue. Nencki also supposed that the presence of products of fermentation stopped all action of the organisms. To controvert this statement, Gunning adduces experiments which were already in progress before Nencki had published his objections. These consisted in keeping putrefying matter in tubes in which oxygen, hydrogen, and air were enclosed. As was to be expected, fermentation proceeded furthest in the tubes containing pure oxygen, less far in those containing air, and very much less in those containing hydrogen. The amount of decomposition was ascertained by estimating the carbonic anhydride, ammonia, and volatile acids. Nencki's last objection was that by some chance the liquids infected may have come in contact with only those bacteria which require oxygen for their existence. This objection is shown by Gunning to depend on a misunderstanding of Pasteur's researches, viz., that two such varieties exist. Pasteur believes that such ferments as exist at the surface of a putrefying medium obtain oxygen from the air, and those in the interior of the liquid derive oxygen from the decomposing substance, but does not imagine two varieties to exist. Besides, even were there such different organisms, it is impossible to believe that from some chance a liquid should become infected with only one variety, and that the germs of the other variety, which would be just as likely to be present in air to the same extent, should have no influence. W. R.

**Nitrification.** By T. SCHLOESING, and A. MUNTZ (*Compt. rend.*, 89, 891—894, 1074—1077).—For the preceding researches of the same authors see this Journal, 34, 597. The authors have separated the organism producing nitrification from the other organisms existing



in soil by systematic cultivation in suitable solutions, which had been previously sterilised by heat. The nitrifying organism consists of minute corpuscles, round or slightly elongated; they occur frequently in pairs, and appear to propagate by budding; they are not easily distinguished from other organisms of the same class.

The nitrifying organism is somewhat easily destroyed by heat; exposure for ten minutes to  $100^{\circ}$  is certainly fatal, and even  $90^{\circ}$  is generally sufficient. Desiccation also arrests nitrification, and apparently kills the ferment. A soil actively nitrifying may be effectually sterilised by drying at the temperature of the air. Long deprivation of oxygen also kills the ferment, at least in liquid mediums. In mediums rich in organic matter, *mucor* is its chief enemy. Until the life of the fungus has run its course, no nitrification will occur.

The nitrifying organism is not normally present in the air. In no case has nitrification been started in a sterilised solution by the access of ordinary air. It is abundant in soil, in sewage, and in waters contaminated with organic matter. In running water, it is sparsely distributed, attaching itself to the surfaces of solid bodies. It collects at the bottom of the vessel, when the water is allowed to rest.

The effect of temperature on nitrification in liquid mediums was ascertained. Below  $5^{\circ}$  the action is extremely feeble; it becomes appreciable at about  $12^{\circ}$ . With a rising temperature, the action rapidly increases, reaching its maximum at  $37^{\circ}$ , at which point the production of nitrates is ten times as rapid as at  $14^{\circ}$ . Beyond  $37^{\circ}$ , a speedy diminution of action takes place; at  $45^{\circ}$ , less nitrate is formed than at  $15^{\circ}$ ; and at  $50^{\circ}$ , the action is very slight. Beyond  $55^{\circ}$ , no nitrification occurs.

Free access of oxygen is essential for rapid nitrification. Other conditions being equal, nitrification in liquids will be in proportion to the surface exposed. In soils, nitrification will be greater in proportion to the amount of water present, up to that point at which the pores of the soil become filled and air excluded. Feeble alkalinity is another essential condition. This condition is generally satisfied by the presence of carbonate of calcium, but may also be fulfilled by alkali carbonates, including carbonate of ammonium; if, however, the amount of alkali carbonate exceeds two or three thousandths of the solution, nitrification is arrested. Small quantities of neutral salts are without effect. Sugar, glycerol, alcohol, tartrates, and albumin are all capable of furnishing the organic carbon required by the organism. There is no constant relation between the carbonic and nitric acids produced. Strong light is prejudicial to nitrification, but feeble illumination has little effect.

Nitrites are seldom formed in soils, but frequently in liquids if the temperature is below  $20^{\circ}$ , or the access of air is limited. A thin layer of liquid may produce nitrates, and a thicker layer nitrites.

R. W.

*Note by Abstractor.*—At Rothamsted, the maximum temperature at which nitrification occurs was found to be much lower than here stated. Solutions kept for 54 days at  $40^{\circ}$  refused to nitrify though twice seeded. The difference may perhaps be explained by the different depths of the solutions; this at Rothamsted was about five

inches, and in the case of the above experiments was (apparently) but a few millimeters. The production of nitric or nitrous acid is shown by the Rothamsted experiments to be determined in some cases by the condition of the ferment, rather than by the conditions of the medium.

R. W.

**Nitrification.** By E. W. DAVY (*Chem. News*, 40, 271).—Experiments were made in reference to the addition of animal impurities in potable waters, and to ascertain the circumstances which were favourable or otherwise to the formation of nitrites and nitrates in waters, which were so polluted. By using Price's well-known test for nitrites, the author in most cases obtained the evidence of the formation of nitrites.

Warington concludes from some experiments made that darkness is an essential condition to the development of those low forms of vegetable life which are supposed in many instances to give rise to nitrification, but from the results of several comparative experiments made in this way, the author came to the conclusion that the condition of light or darkness exercises but little influence one way or the other in this process.

The author mentions that as regards nitrification occurring in water containing organic matters, it is necessary to have a certain amount of air or free oxygen to carry on the process. It was also found that the quantity of animal matter which is held in solution in the water exercises a considerable influence on nitrification; the influence of temperature, however, is still greater, for it has been observed that in cold weather nitrification is very slow, whilst in warm weather, it is much quicker, and that by the application of artificial heat, the process can be greatly accelerated.

In conclusion, the author calls attention to another fact noticed in connection with this subject, viz., the rapidity with which nitrites are sometimes formed in water contaminated with sewage impurities.

D. B.

**Albumin and Amido-compounds in Plants.** By O. KELLNER (*Bied. Centr.*, 1879, 671—676).—The author made a series of investigations on plants at different stages of their growth with respect to the amount of albumin and amido-compounds they contain. His results confirm conclusions already arrived at (*Bied. Centr.*, 1879, 370; this Journal, 1879, Abst., 819), namely, that the amount of albumin reaches its maximum only when the plant has arrived at full maturity. With regard to the conversion of nitrogen from inorganic sources into albumin, the author finds that with nitrates, a certain quantity is converted into amido-compounds. The plant investigated was the common pea. After soaking the seeds in water, they were divided into three lots, and sown in sand, the first lot being treated regularly with distilled water, the second with solution of nitre, and the third with a solution of ammonium nitrate.

Nine different kinds of potatoes grown on unmanured land gave the following mean results on analysis:—

|                  | Percentage of<br>dried substance. | Percentage of nitrogen<br>in dried substance. | Percentage of<br>nitrogenous albumin in total. |
|------------------|-----------------------------------|---|--|
| Nos. 1—5 . . . . | 19.45                             | 2.117   | 49.1   |
| „ 6—9 . . . .    | 22.29                             | 1.619   | 57.1   |

These figures show that the total quantity of nitrogen decreases as the total solid matter increases, while the albumin undergoes not merely a relative, but also an absolute increase. J. K. C.

**Resistance of Seeds to the Prolonged Action of Chemical Agents.** By I. GIGLIOLI (*Gazzetta*, 9, 474—505).—The seeds employed in this research were chiefly those of lucerne, as they offer great resistance to the action of reagents, and germinate quickly. They were carefully selected, and trial experiments made during the course of the investigation showed that 90 per cent. germinated under favourable conditions. In all the experiments, the seeds were sown in quartzose sand kept moist.

*Action of Gases*.—The seeds, either dry or moist, were placed in a glass globe furnished with two tubes, through which a current of the gas was passed until the air was entirely expelled, when the orifices were hermetically sealed. The gases employed were oxygen, nitrogen, hydrogen, carbonic oxide, carbonic anhydride, methane, nitrous oxide, nitric oxide, ammonia, sulphurous anhydride, hydrogen sulphide, chlorine, hydrochloric acid, and arseniuretted hydrogen, and the time during which the seeds were left in contact with the gas varied from 1 to 593 days. Full details of the experiments are given, and from the results the author infers that all seeds do not resist the action of the same gas equally well, those being least affected which, like lucerne, have an involucre not easily permeable by gases. If softened in water, they invariably die when exposed to the action of any other gas than air, and that whatever may be the structure of the involucre.

Of the different gases, chlorine, hydrochloric acid, and ammonia act comparatively rapidly on seeds normally dry, although these may be able to resist the action of nitric oxide, sulphurous anhydride, and hydrogen sulphide for a considerable time, whilst the other gases act but slowly on them; moreover, those seeds which have resisted for a long time the action of the more energetic gases do not germinate in the normal manner, the root being but slightly developed if at all, and the cotyledons are often green.

*Action of Liquids*.—The author had completed his investigation of the action of liquids on seeds before the publication of Nobbo's results. These he can confirm by his own observations, which embrace a much wider field, and include the action of water, methylic, ethylic, and amyllic alcohol, ether, chloroform, carbon tetrachloride, carbon bisulphide, ethyl iodide, glycerol, benzene, nitrobenzene, and aniline, both at the ordinary temperature and at their boiling point, the seeds being dry in some cases, and in others previously steeped in water. The results show that various kinds of seed differ in their power of resisting the action of liquids, this depending exclusively on the structure of the integument. Of the seeds tried, lucerne is least

affected, whilst the vitality of wheat is most easily destroyed. Of all the liquids employed, water is the most readily absorbed, and it is the only one which causes the seeds to swell; moreover, if the other conditions for germination are wanting, it is the liquid which most quickly destroys the vitality of the seed. Seeds which have been steeped rapidly lose their power of germination in contact with other liquids. When the temperature of ebullition is comparatively low, as is the case with ether and carbon bisulphide, the seeds with sensibly impermeable involucre, such as those of lucerne, can resist the action of the boiling liquid for a long time, no appreciable quantity of fatty or waxy substance being extracted.

*Action of Solutions.*—Alcoholic solutions of iodine, of potassium bromide, sulphide, and cyanide, of zinc and mercuric chlorides, copper sulphate, ammonium sulphide, arsenious anhydride, camphor, and phenol were tried, using seeds of lucerne and wheat. It was found that the latter were rapidly killed (except when treated with a glycerol solution of copper sulphate) whilst the lucerne resisted the action of most of the solutions for a long time. They were, however, quickly destroyed by alcoholic solution of iodine when concentrated, by potassium and ammonium sulphides, and by an alcoholic solution of sulphurous anhydride.

C. E. G.

**Mode of Action of Sulphur as a Remedy against Vine-disease.** By J. MORITZ (*Ber.*, 12, 1938).—The efficacy of sulphur in protecting vines against the destructive attacks of the fungus *Oidium Tuckeri* is due to the evolution of sulphurous anhydride, which occurs when that substance is sprinkled over the living vine.

T. C.

*Note.*—Pollacci (this Journal, 1876, ii, 540) states that *hydrogen sulphide* is produced when vines are sulphured, and that it is to this that the destruction of the *oidium* is due.—C. E. G.

**Analysis of Soils from the Bunter Sandstone Formation.** By R. WEBER (*Bied. Centr.*, 1179, 650—651).—The soils under investigation were produced by the weathering of bunter sandstone from Spessart and Vogesen. Samples were taken from poor and good plots, and analyses were made from the surface and subsoil of each. The author finds that the upper layers of soil taken from plots planted with oak and beech contain more humus than is the case when the ground is overgrown with fir; also that soils from the latter yield less potash when treated with hydrochloric acid, and contain only about one-half the amount of soluble silica present in the former case. It is also remarkable that the quantity of phosphoric acid present is in direct proportion to the fertility of the soil.

J. K. C.

## Analytical Chemistry.

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### Application of the Galvanic Current in Analytical Chemistry.

By C. LUCKOW (*Zeits. Anal. Chem.*, 1880, 1—19).—The subject is divided into—(1) the qualitative behaviour of various soluble and insoluble compounds of the commonly occurring elements under the influence of the galvanic current, and (2) the electrolytic quantitative separation and estimation of various metals, partly in the metallic state and partly in the state of compounds of constant composition. Either a constant battery or a thermo-electric pile is used for the production of the electricity. Of all constant batteries Meidinger's is most suitable for analytical purposes (*ibid.*, 8, 31). Among thermo-electric piles, Clamond's, in the form of a cylinder, using gas, petroleum, or charcoal, is best (*ibid.*, 15, 334). A voltameter is used to measure the strength of current.

(1.) *The Qualitative Behaviour of various Soluble and Insoluble Compounds of the commonly occurring Elements under the influence of the Galvanic Current.*—The action is different, according as it takes place in a simple cell, in which both poles are immersed, or in a divided cell. The strength of the current, the concentration and temperature of the solutions, also in some cases influence the nature of the decomposition. In the simple cell, the products of decomposition are allowed to freely mix with each other and hence secondary products arise.

The galvanic current in acid solutions has mainly a reducing, and in alkaline solutions an oxidising action. For instance, a solution of potassium chromate acidified with sulphuric acid is reduced when in the simple cell, all the chromic anhydride being converted into chromic oxide, whilst a solution of chromic oxide in potassium hydrate is converted into potassium chromate.

In the electrolysis of cyanides, the cyanogen undergoes a further decomposition, the final products consisting of carbonic anhydride and nitrogen. Prussian blue is deposited on the positive pole from solutions of ferro- and ferri-cyanides. In dilute solutions of metallic chlorides, hypochlorous acid is alone produced, in concentrated solutions chlorine is also liberated; chlorates are produced from the chlorides of the alkalis and alkaline earths as soon as the reaction of the solutions has become alkaline, from the evolution of the chlorine and hypochlorous acid.

If dilute chloride solutions contain a little free hydrochloric acid, hypochlorous acid is alone produced, and the solution after a time acquires an alkaline reaction. Iodine and bromine are separated from solutions of iodides and bromides. Iodates and bromates are produced simultaneously from the iodides and bromides of the metals of the first two groups, especially in concentrated solutions. Potassium cyanide is decomposed by the galvanic current into potassium and ammonium carbonates. When the solutions of the chlorides, bromides, and iodides contain free alkali, only chlorates, bromates, and iodates are produced. From the insoluble compounds of chlorine, bromine, iodine, cyanogen, ferro-, and ferri-cyanogen with the metals suspended

in dilute sulphuric or nitric acids, the metal is separated at the negative pole, whilst the acid radicle appears at the positive.

Concentrated nitric acid is decomposed with production of nitrous acid; in the acid of sp. gr. 1.2, this decomposition does not occur, at all events under the influence of a feeble current. No ammonia is produced from dilute nitric acid, either *per se* or in presence of sulphuric acid; but if a solution of cupric sulphate is added in sufficient quantity, ammonium sulphate and metallic copper are produced simultaneously until all the nitric acid is converted into ammonium sulphate. In the presence of free alkali, nitrates are not converted into ammonia, but the latter is converted to nitric acid. Concentrated (English) sulphuric acid is decomposed with deposition of sulphur. Sulphurous acid in aqueous solution decomposes into sulphur and sulphuretted hydrogen; the sulphites are gradually converted into sulphates. Thiosulphates are converted into their corresponding sulphates with separation of sulphur. The alkaline sulphides, according to their richness in sulphur, are decomposed with or without separation of sulphur, sulphates being formed. In the alkaline sulphates and thiosulphates, in addition to sulphides, polythionates are always produced. Phosphoric acid or phosphates undergo no change in dilute solutions. Carbonic anhydride is very incompletely evolved at the positive pole from the solutions of hydrogen potassium carbonate. Silicic and boric anhydrides are separated from their concentrated solutions in tree-like crystals at the positive pole.

The metals of the sixth group are all separated from their solutions by the galvanic current in the metallic form. In the electrolysis of the chlorides of antimony and arsenic, some antimoniuiretted and arseniuiretted hydrogen are produced at the negative pole. If the three metals occur together, first arsenic, then antimony, and lastly tin is precipitated. Platinum is deposited from its solutions in the reguline form at first, but as the solutions become more dilute, in the form of platinum black. From the solution of their sulphides in alkaline sulphides, tin and antimony are separated completely, arsenic not quite completely, in the metallic form. The oxide of tin produced by the action of nitric acid, and the oxide of antimony formed in the same way, dissolve on heating in concentrated potash or soda: the metallic separation from these solutions is very incomplete, unless sulphuretted hydrogen is passed into the alkaline solutions or they are acidified with hydrochloric acid.

Of the metals of the fifth group, copper is precipitated from solutions containing free sulphuric, nitric, or acetic acid when the amount of acid in the solution, calculated as anhydride, does not exceed 8 per cent. Also all copper is separated from solutions containing free hydrochloric acid, on the addition of ammonium or sodium chlorides or sodium acetate. Similarly from solutions containing excess of ammonia, ammonium carbonate, or potassium cyanide.

Silver is separated from solutions containing 8—10 per cent. nitric acid in a very bulky metallic state; at the same time some peroxide is precipitated on the positive pole, which, however, can be prevented by the addition of glycerol, sugar of milk, or tartaric acid. From the ammonia or ammonium carbonate solutions, the metal is precipitated

in a very bulky form, peroxide being deposited at the positive pole; this, however, is soon reduced to the metallic state. From potassium cyanide solutions, the silver separates in the metallic form with a dull lustre.

Mercury is precipitated in the form of drops from all its salts; in presence of other metals, amalgams are formed.

Lead is precipitated from neutral solutions partly as metal at the — pole, partly as peroxide at the + pole. A pure metallic separation occurs only in the presence of easily oxidisable substances which prevent the formation of the peroxide. From alkaline solutions, the lead is separated as metal only, in a somewhat bulky form; a slight separation of the peroxide occurs in a pure lead solution only in the presence of not more than 10 per cent. of free nitric acid. If the solution contains copper, even in very small quantities, in addition to lead, all the lead is separated as peroxide in presence of smaller quantities of free acid. Other metals, as silver and mercury, behave in a similar manner, but carry some lead down with them.

Bismuth is precipitated in the metallic state from its solution in presence of free nitric acid, some peroxide being formed at the same time.

Cadmium is completely precipitated from its acid or ammoniacal solution in the metallic state.

If all the above-mentioned metals of the fifth group are present simultaneously, mercury and silver are first precipitated, bismuth and copper only after the greater portion of the first two mentioned metals is separated.

Of the metals of the fourth group, zinc, nickel, and cobalt are incompletely separated in the metallic form, from their sulphates in neutral solution, manganese and uranium not at all. On the addition of potassium acetate, tartrate, or citrate, zinc, nickel, and cobalt separate completely, uranium to a slight extent. In the electrolysis of the ammoniacal or potassium cyanide solution of cyanides, both zinc, nickel, and cobalt, are completely separated. Zinc is furthermore completely separated in the metallic state from its potash solution, to which some potassium cyanide has been added.

Manganese is not separated in the metallic state from its neutral or acid solution, but is deposited as hydrated manganese peroxide. In very dilute solutions of manganese containing much nitric or a mixture of nitric and sulphuric acids, permanganic acid is formed, and imparts its characteristic red colour to the solution.

Uranium is obtained in small quantity only, even from the completely neutral solutions of the oxide, as a yellowish-grey metallic precipitate, soluble in hydrochloric acid.

Iron is incompletely separated in the metallic form from neutral solutions of ferrous salts, some ferric salt being formed. If to the neutral solution of ferrous sulphate, some ammonium citrate be added containing free citric acid, and care be taken that free citric acid remains in the solution, the iron will be deposited in the lustrous metallic form, even when a portion of the iron was present originally in the ferric state. No iron is separated from potassium ferrocyanide, but Prussian blue at the — pole. From the solution of ferrous oxide

in sodium thio-sulphate all the iron is separated, chiefly as ferrous sulphide. From the fluoride dissolved in sodium fluoride, metallic iron is precipitated.

The solutions of the metals of the first three groups offer but few characteristics.

The alkaline earths are distinguished from the alkalis by the production of precipitates of their carbonates on the electrolysis of their salts of organic acids in neutral or slightly acid solutions.

In the solutions of ammonium salts, ammonia is produced at the negative pole.

F. L. T.

**Estimation of Chlorine in Grains and Forage.** By R. NOLTE (*Compt. rend.*, 89, 955—956).—In estimating chlorine in grain, the author finds it necessary to neutralise the phosphoric acid liberated on ignition by adding sodium carbonate before ignition; otherwise the chlorine is evolved. The table which follows shows comparative results with and without the use of sodium carbonate:—

|                    | Without $\text{Na}_2\text{CO}_3$ . | With $\text{Na}_2\text{CO}_3$ . |
|--------------------|------------------------------------|---------------------------------|
| Oats .....         | 0.016                              | 0.0605                          |
| Wheat .....        | 0.007                              | 0.0680                          |
| French beans ..... | 0.0345                             | 0.0455                          |
| Maize .....        | 0.00                               | 0.037                           |
| Barley .....       | 0.0135                             | 0.0396                          |
| Buckwheat .....    | 0.021                              | 0.026                           |
| Rye .....          | 0.006                              | 0.054                           |
| Bran .....         | 0.00                               | 0.080                           |

W. R.

**Method for the Detection and Estimation of Iodine in Presence of Chlorine and Bromine.** By E. DONATH (*Zeits. Anal. Chem.*, 1880, 19—23).—The author was led to the present process from some observations of C. Zulkowsky in a paper "On an Iodometric Estimation of Chromic Acid" (*J. pr. Chem.*, 103, 351). The process consists in the distillation of the mixed chlorides, bromides, and iodides with chromic acid solution, when the chlorides are found to be entirely and the bromides almost entirely unacted on, especially in dilute solution, the iodides being decomposed according to the equation  $6\text{KI} + 8\text{CrO}_3 = \text{I}_2 + \text{Cr}_2\text{O}_3 + 3\text{K}_2\text{Cr}_2\text{O}_7$ , the resulting iodine being collected in a solution of potassium iodide and determined in the usual manner.

F. L. T.

**Titration of Iodine by Stable Standard Solutions.** By E. ALLARY (*Bull. Soc. Chim.* [2], 32, 273—276).—The author's process is a modification of that proposed by Pellieux and Allary, in which bromine is made to replace combined iodine, which is removed as fast as liberated by agitation with carbon bisulphide, the termination of the reaction being reached when, after an addition of the bromine solution, a fresh drop of carbon bisulphide ceases to be tinged violet. In place of the alterable solution of free bromine, the author uses a solution containing a definite mixture of alkaline bromate and bromide, which is easily prepared, and may be kept any length of time



without alteration in strength. This solution is made to act upon the iodide to be determined, in the presence of free hydrochloric acid, when the following reactions take place:— $5\text{KBr} + \text{KBrO}_3 + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + 6\text{Br}$  and  $6\text{KI} + 6\text{Br} = 6\text{KBr} + 6\text{I}$ . The liberated iodine is transformed into bromide of iodine by continued addition of the bromated solution, and starch-paste is used as an indicator. The mixture of bromate and bromide is made by saturating a concentrated solution of pure sodium hydrate with excess of pure bromine, and evaporating to dryness, without igniting. Two grams of this saline mixture are dissolved in water and made up to 1 litre. The standard solution of potassium iodide contains 1.308 gram of the pure salt (= 1.000 gram iodine) in 1 litre. The starch solution is made according to Mohr's formula. To standardise the bromated solution, 10 c.c. of the standard potassium iodide are measured into a test-glass, and an excess of pure hydrochloric acid added, together with a few drops of starch solution. The bromated solution is now run in cautiously from a burette, with constant stirring. The liquid is successively coloured blue, the tint of wine lees, cinnamon, and very pale yellow. The point of maximum decoloration is easily seen, and the reading should be confirmed by adding a very slight excess of the bromated liquid, and titrating back with standard potassium iodide, added drop by drop until the slightest deepening of tint is observed. The strength of the bromated solution should be adjusted so that 1 c.c. = 1 c.c. of the standard potassio-iodide. If free iodine has to be estimated by this method, it should be transformed into hydriodic acid by addition of sulphurous acid. Iodic acid may be reduced to hydriodic acid by the same reagent. The author describes the application of this method to the determination of the iodine in kelp.

J. M. H. M.

#### Separation of Phosphoric Acid from Iron and Aluminium.

By P. DEROME (*Compt. rend.*, 89, 952—953).—The substance containing phosphoric acid is mixed with five or six times its weight of dry sodium sulphate, and strongly ignited for ten minutes. On cooling, the mass is treated with water, when the phosphoric acid all dissolves as tribasic sodium phosphate, the iron and aluminium remaining as oxides. The exactness of this process is attested by numerous analyses.

W. R.

**New Process for Analysing Commercial Potash.** By B. CORENWINDER and G. CONTAMINE (*Compt. rend.*, 89, 907—908).—This process is to acidify the solution with hydrochloric acid, add platinic chloride, and evaporate. The potassio-platinic chloride is washed with alcohol and ether, and then dissolved on the filter with hot water. The platinum in the solution is reduced to the metallic state with a hot solution of sodium formate, and is weighed as such. The advantage is that it is unnecessary to remove sulphuric and phosphoric acids and silica from the potash before precipitation with platinic chlorides.

W. R.

**Detection of Cobalt and Nickel in presence of each Other.** By G. PAPASOGLI (*Gazzetta*, 9, 509—513).—The author has observed

that when a plate of zinc is immersed in a solution of the double cyanide of nickel and potassium, hydrogen is evolved, and metallic nickel is deposited on the plate as a black powder; at the same time a dense cloud of a deep red-coloured liquid is formed around the latter, and gradually sinks to the bottom, until finally the whole liquid becomes of a blood-red colour. No such phenomenon takes place with the corresponding cobalt compound.

In order to test an acid solution containing the two metals, a slight excess of potash is first added, so as to precipitate the metals as basic salts; these are well washed by decantation, and after adding a little ammonium chloride solution and ammonia, the precipitate is dissolved in a very slight excess of a concentrated solution of potassium cyanide, taking care to avoid agitation as far as possible, to prevent the double cobalt cyanide from absorbing oxygen from the air. The solution is then divided into two parts, one of which is tested for cobalt in the manner previously suggested by the author, that is, by adding a few drops of ammonium polysulphide, so that it may float on the cyanide solution; if cobalt be present, an intense red coloration will be seen at the point of contact of the two liquids. This reaction is very sensitive, and quite independent of the presence of nickel. To test for nickel, a plate of zinc is immersed in the other portion of the cyanide solution, when, if it be present, an evolution of gas will take place, and the red coloration above mentioned will be observed. This reaction is not interfered with by the presence of cobalt; but if too much cyanide has been used to dissolve the basic salts, a violent evolution of gas will take place from the zinc plate, which disperses the red-coloured liquid formed at its surface, and renders it impossible to detect the presence of the nickel if the quantity is but small.

C. E. G.

**New Method of Separating Nickel from Cobalt.** By P. DREVELL (*Compt. rend.*, 89, 903—905).—This process depends on the fact that a solution of microcosmic salt, saturated in the cold, mixed with a solution of ammonium bicarbonate saturated with carbonic acid, produces with salts of cobalt a bluish precipitate; after boiling for some seconds, a few c.c. of ammonia are added, and on heating to 100°, all the cobalt is precipitated as  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , which is changed to  $\text{Co}_3\text{PO}_7$  on ignition. If nickel is present, the whole of it remains in solution, as nickel salts give a blue colour, but no precipitate. The nickel remaining after separation of cobalt may be precipitated as sulphide. Full details of the method for separating the two metals are given. In a note appended to this paper, Pisani states that ammonium acetate may be substituted for ammonium carbonate.

W. R.

**Estimation of Cobalt and Nickel.** By E. DONATE (*Ber.*, 12, 1868—1869).—This method is a modification of Fleischer's (*J. pr. Chem.*, 1870, Bd. 2, 48), and depends on the fact that when a solution of a cobalt salt is heated with potash or soda and iodine, cobalt sesquioxide is formed, whilst nickel salts are not changed. Therefore, in order to determine both the cobalt and nickel, the solution containing the two metals is divided into half, one half is boiled with potash and bromine, which precipitates both the cobalt and nickel, and the other half with

potash and iodine, whereby the cobalt alone is thrown down. The sesquioxides thus obtained are in each case heated with hydrochloric acid, and the liberated chlorine passed into potassium iodide solution, and finally the free iodine determined by titration with decinormal sodium thiosulphate solution. From the equation,  $\text{R}_2\text{O}_3 + 6\text{HCl} = 2\text{RCl}_3 + 3\text{H}_2\text{O} + \text{Cl}_2$ , it is seen that 1 atom of iodine equals 1 atom of cobalt or nickel. Further, as the atomic weight of each metal is 59, so the difference of c.c. of decinormal thiosulphate solutions used in the two cases, when multiplied by 0.0059, gives the quantity of nickel. And the number of c.c. used in the second case, multiplied by 0.0059 gives the quantity of cobalt. P. P. B.

**Estimation of Chromium and Tungsten in Steel, and in their Alloys with Iron.** By R. SCHOFFEL (*Ber.*, 12, 1868—1867).—*Estimation of Chromium.*—The material finely powdered in a steel mortar is treated with a solution of the double chloride of copper and sodium or ammonium, by which means the greater portion of the iron is removed and a porous mass is left containing the chromium: the chromium is determined in this by fusion with sodium carbonate and nitre, extraction with water, and after carefully neutralising the filtrate with nitric acid, precipitating the chromate by mercurous nitrate. When silica is present, the aqueous solution obtained by extracting the fused mass is acidified with hydrochloric acid, a little alcohol added, and the whole evaporated to dryness: in the filtrate from the silica the chromium is precipitated by means of ammonia.

The above method is not applicable in cases where the amount of chromium present is more than 8 per cent., as then the residue left after treatment with the double chlorides of copper and sodium is not easily oxidised by fusion. In such cases, it is better first to digest the steel with concentrated hydrochloric acid; the insoluble portion is then fused with sodium carbonate and nitre, and the solution of the fused mass in hydrochloric acid added to the hydrochloric acid solution of the steel. To separate the iron and chromium in such a solution, the author uses a method similar to that described by W. J. Sell (*Ber.*, 12, 847), which consists in almost neutralising with sodium carbonate, and after adding sodium acetate solution, which must not produce a precipitate, the solution is boiled with potassium permanganate solution. Thus the greater portion of the iron separates out, and the supernatant liquid must have a red colour, indicating the presence of an excess of permanganate, which excess is destroyed by means of alcohol, and sodium carbonate is added to precipitate all the iron. In the filtrate from the iron, the chromium exists as chromate. A similar result is more advantageously obtained by using bromine instead of potassium permanganate.

*Estimation of Tungsten.*—The estimation of this element may be made in a manner similar to the above; the residue obtained by treating the steel with solution of the double chlorides of copper and ammonium, is fused with sodium carbonate. The aqueous extract of the fused mass is neutralised with nitric acid and the tungstate precipitated by mercurous nitrate. If silica is present, then the weighed tungstic acid is fused with potassium hydrogen sulphate, and the weight of the

silica left on extracting the fused mass with water, deducted from the first weighing, gives the weight of tungstic acid. When the amount of tungsten is higher than 12 per cent., it is better to digest the material with aqua regia, a portion of the tungsten then going into solution, whilst some separates out as tungstic acid; if the solution is allowed to stand for some days, the whole of the tungsten separates out, and may be filtered off, and the residue fused with sodium carbonate and treated as above. In case of an alloy containing 10 per cent. of tungsten, aqua regia does not produce a complete solution, but yields a black residue containing some tungstic acid, which is, however, decomposed by fusion with sodium carbonate. P. P. B.

**Influence of Acetic Acid on the Separation of Iron as Basic Acetate from Manganese, Zinc, Cobalt, and Nickel.** By J. JEWETT (*Chem. News*, 40, 273).—It has often been observed, when manganese is separated from iron by precipitating the latter as a basic ferric acetate, that some manganese is carried down with the iron precipitate. Eggertz states that this can be obviated, at least to a great extent, by the presence of free acid. The author experimented in this direction and found that the presence of free acid decreased the amount of manganese in the iron precipitate, but at the same time prevented complete precipitation of the iron. A series of experiments, in which the only variable factor was the acetic acid, was undertaken to ascertain to what extent free acetic acid is efficient in keeping manganese, likewise zinc, nickel and cobalt, in solution, when present in quantities not too great to prevent precipitation and washing of the iron. It was found that, by using 4 per cent. of volume of acetic acid (sp. gr. 1.044) and adhering to the necessary precautions of the process, a complete separation by one precipitation can be obtained of zinc, and one sufficiently accurate for most purposes of manganese, whilst the amount of nickel and cobalt that goes down with the iron lessens with increase of acetic acid. D. B.

**New Method of Separating Manganese and Iron.** By BELLSSTEIN and JAWHIN (*Ber.*, 12, 1487).—Iodine is added to the solution, previously treated with potassium cyanide in excess, when the manganese is precipitated as peroxide. Ch. B.

**Estimation of Carbon in Cast-Steel.** By S. KEEN (*Chem. News*, 40, 225).—The following analyses show the difference in Eggertz's method and the combustion method, in estimating the amount of carbon in steels. For the combustion method, chromic acid was used:—

|                   |      |      |      |      |      |      |      |      |
|-------------------|------|------|------|------|------|------|------|------|
| Combustion used.. | 0.14 | 0.17 | 0.27 | 0.38 | 0.37 | 0.46 | 0.64 | 1.02 |
| Eggertz's method  | 0.12 | 0.15 | 0.24 | 0.34 | 0.36 | 0.45 | 0.60 | 1.03 |

D. B.

**Clarke's Method for the Separation of Tin from Arsenic and Antimony.** By F. P. DEWEY (*Chem. News*, 40, 257—259).—In experimenting on the separation of tin, arsenic, and antimony, the author decided to make a thorough investigation of the method proposed

by Clarke as the most favourable. Owing to the want of time, the separation of tin from antimony was the only one that could be undertaken. Some qualitative experiments were made to test the influence of free hydrochloric acid on the separation, and also the statement of Clarke that antimony could not be detected in the filtrate from the antimony trisulphide, either by the Marsh test or the black stain on platinum with zinc, and that oxalic acid did not interfere with either of these tests. It was found that, to get the best separation, no hydrochloric acid should be present, although a very small amount does not exert any very great solvent action on the antimony trisulphide. Oxalic acid obscured the platinum and zinc test, forming a dense white coating on both the platinum and zinc when the acid became nearly neutralised; this completely masked any black stain that might have been produced on the platinum. It did not, however, obscure the Marsh test in the least. Another series of experiments showed that solutions of stannic chloride and antimony trichloride containing free hydrochloric or nitric acid, or both, can be safely evaporated to dryness if a sufficient amount of potassium chloride is present.

Other points of minor importance are considered in the original paper.  
D. B.

**Methods for Indicating the Presence of Organic Matter in Water.** By F. TIEMANN and C. PREUSSE (*Ber.*, 12, 1906—1924).—The authors have submitted some of the various methods proposed for this purpose to a critical examination, with the following results:—

I. *Determination by Ignition of the Solid Residues dried at 180°.*—To this method it is objected that (1) the organic matter not expelled by evaporation is alone taken into account. (2) Silica present displaces carbonic acid, and this is not again taken up on evaporation with ammonium carbonate. (3) Different mineral matter will retain different amounts of moisture at 180°. (4) Some of the chlorides of the alkalis will be volatilised. Finally, the organic matter will react on the inorganic matter present, *e.g.*, decomposing nitrates and nitrites into cyanates and cyanides.

II. *Frankland and Armstrong's*, and III. *Dittmar and Robinson's* (*Chem. News*, 1877, 26).—To these methods the authors raise the objections that they do not take into consideration the organic matter volatilised by boiling in acid solution, nor the decomposition which the organic matter undergoes by evaporation in presence of sulphurous acid and ferrous chloride. Further, since the amount of carbon and nitrogen differs in organic compounds, this method gives no evidence of the absolute quantity of organic matter present; and only comparative results, when the mixture of the organic compounds in the waters compared is similar. This latter objection applies also to the following methods.

IV. *Methods in which Potassium Permanganate is used as an Indicator.*—(a.) Kubel's method (Kubel-Tiemann, *Anleit. zur Untersuchung von Wasser*, II Aufl., 104). The water is acidified with sulphuric acid, and boiled with a quantity of centinormal potassium permanganate solution for 10 minutes; the unused permanganate is destroyed by centinormal oxalic acid; and the excess of oxalic acid is determined by titration with permanganate solution. Thus the amount of potassium

permanganate reduced by the organic matter is determined and consequently the oxygen required for the latter's oxidation.

(b) Schulze's method (*ibid.*, 102). This method differs from Kubel's, inasmuch as the water is rendered alkaline by adding a little soda, instead of being acidified with sulphuric acid. After boiling for ten minutes, the water is acidified with sulphuric acid, and the amount of unused potassium permanganate determined as before.

(c.) Tidy's method (this Journal, *Trans.*, 1879, 66).

The advantage of these methods is that both the volatile and the non-volatile organic matter is taken into consideration. Of the three methods the authors prefer that of Kubel, as being the most free from sources of error, and at the same time the simplest.

V. Fleck's method (*J. pr. Chem.* 4, 364). The oxidising agent used in this method is a solution of silver nitrate in sodium thiosulphate, made alkaline by soda. The water is boiled with this solution for ten minutes, and the silver in solution determined by titrating with a  $\frac{1}{10}$  normal solution of potassium iodide. The end of the reaction is reached when a drop of the solution, added to a drop of a mixture of hydrochloric acid, potassium permanganate, and starch-paste, produces a blue coloration.

The authors have made a series of experiments with solutions of various organic bodies, in order to compare the methods of Kubel and Fleck. The results obtained show that organic matter reduces potassium permanganate more quickly than the alkaline silver solution. Fleck claims that his method indicates the presence of volatile organic matter very delicately. These two methods have been compared with water saturated with coal gas, the result being that Kubel's method is judged the better of the two.

In order to settle the question whether the organic products of fermentation reduce potassium permanganate more strongly than the bodies from which they are formed, the authors have made the following experiments:—A dilute solution of albumin was titrated with permanganate solution when freshly made, and then after putrefaction had taken place. These experiments indicated that the products of putrefaction have a slightly stronger reducing action than the original compound.

In order to settle the question of the presence of volatile organic matter in waters, the authors have made experiments with some of the waters in Berlin, the mode of procedure being to distil the water alone, (2) after acidifying with sulphuric acid, and (3) after making it alkaline by the addition of soda.

The following results were yielded by the water of a brook in the north-west of Berlin:—

100 c.c. of the water reduce 41.98 mgrm.  $\text{KMnO}_4$  = 10.62 mgrm.

(a.) *Distillation of the Neutral Water.*

|      |                   |            |                 |   |            |    |
|------|-------------------|------------|-----------------|---|------------|----|
| 1st. | 100 c.c. required | 5.05 mgrm. | $\text{KMnO}_4$ | = | 1.28 mgrm. | O. |
| 2nd. | "                 | 2.59       | "               | = | 0.65       | "  |
| 3rd. | "                 | 1.56       | "               | = | 0.39       | "  |
| 4th. | "                 | 1.06       | "               | = | 0.27       | "  |

(b.) *Distillation of the Acidified Water.*

|      |                   |            |                 |   |            |    |
|------|-------------------|------------|-----------------|---|------------|----|
| 1st. | 100 c.c. required | 4.51 mgrm. | $\text{KMnO}_4$ | = | 1.14 mgrm. | O. |
| 2nd. | "                 | 2.73       | "               | " | = 0.69     | "  |
| 3rd. | "                 | 1.78       | "               | " | = 0.45     | "  |
| 4th. | "                 | 1.61       | "               | " | = 0.4      | "  |

(c.) *Distillation of the Alkaline Water.*

|      |                   |            |                 |   |            |    |
|------|-------------------|------------|-----------------|---|------------|----|
| 1st. | 100 c.c. required | 4.28 mgrm. | $\text{KMnO}_4$ | = | 1.08 mgrm. | O. |
| 2nd. | "                 | 1.92       | "               | " | = 0.48     | "  |
| 3rd. | "                 | 1.07       | "               | " | = 0.27     | "  |
| 4th. | "                 | 1.04       | "               | " | = 0.26     | "  |

As (a) and (c) contain quantities of ammonium salts, the effect which these salts have on potassium permanganate was investigated. As a result, it was found that 100 c.c. of a solution containing 100 mgrms. ammonia required 0.91 mgrm.  $\text{KMnO}_4$ , which is equivalent to 0.24 mgrm. of oxygen; whereas a solution containing 1 mgrm. ammonia in 100 c.c. had no effect.

The disadvantage of Kubel's method is that from it no idea can be formed of the nitrogenous organic matter present; this, however, may be attained by the use of Wanklyn, Chapman and Smith's method of distilling with an alkaline solution of potassium permanganate. This latter method, the authors have tried with solutions of such bodies as quinine sulphate, ethylamine hydrochloride, aniline hydrochloride, aspartic acid, urea, allantoin, leucine, tyrosine, and some others. As a result, the authors find that the ammonia given off is always less than that required by theory; but in such cases as leucine, aspartic acid, and tyrosine-compounds (resulting from the putrefaction of albuminous matter), the quantity of ammonia approaches the theoretical very nearly. The results of this method yield no clue to the absolute quantity of nitrogenous organic matter in a sample of water, and the results obtained in two cases can be compared only when the mixtures of organic compounds in the different waters are similar.

P. P. B.

**Use of the Polariscopes in testing Crude Anthraquinone for Anthracene.** By B. NICKELS (*Chem. News*, 40, 270).—By examining anthracene and anthraquinone with the polariscopes, both compounds are said to present very beautiful objects, the former as crystallised in the tabular form exhibiting a superb play of colours, whilst anthraquinone, similarly viewed, presents coloured bands only, crossing the needles individually or grouped. Other substances accompanying crude anthracene, such as carbazol, acridine, phenanthrene, pyrene, chrysene, &c., also exhibit to some extent distinctive and characteristic forms, but as compared with anthracene, whether as hydrocarbons or oxidised products, so entirely different that limited observation readily distinguishes them. Naphthalene is the only body in any way resembling anthracene, but here again with equally characteristic difference, and to a careful observer there need be no error in judgment.

D. B.

## General and Physical Chemistry.

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**Motion produced by the Diffusion of Gases and Liquids** By ST. CLAIRE-DEVILLE (*Compt. rend.*, 90, 18—22).—If a tube of platinum or cast steel filled with hydrogen is heated to 1000° in an atmosphere of nitrogen, the hydrogen escapes from the tube and a vacuum is produced. If, on the other hand, the tube is filled with nitrogen and exposed to an atmosphere of hydrogen at 1000°, the hydrogen penetrates the platinum or steel, and the pressure inside the tube is equal to 2 atmospheres.

As a second experiment to illustrate the diffusion of gases, a U-tube, 10 meters high, one limb of which has been sealed at the blowpipe, is partly filled with water; the level of the liquid in the two limbs should be identical. The apparatus is placed under a bell-jar, through which a current of ammonia passes; the water in the tube absorbs the ammonia, and finally becomes saturated by it, the ammonia gas then diffuses into the air contained in the closed limb, and increases the pressure until the liquid is forced out of the closed limb.

If the closed limb is filled with ammonia gas, and the other with a saturated solution of ammonia, on exposing the apparatus to the atmosphere, the liquid will gradually rise and fill the closed limb.

The well-known apparatus of Debray for illustrating the diffusion of gases through a porous cell is also described. W. C. W.

**Temperature of Decomposition of Vapours.** By A. WURTZ (*Compt. rend.*, 89, 1062—1065).—In reply to Deville's remarks on the vapour of chloral hydrate, the author quotes the following experiments to show that the vapour is a mixture of water and chloral:—1. The vapour diffuses like a mixture of steam and chloral (Wiedemann and Schulze, *Annalen* [2], 6, 293). 2. The water can be separated from the chloral by distillation (Naumann, *Compt. rend.*, 89, 285). 3. When anhydrous potassium oxalate is heated in the vapour of chloral hydrate, at a temperature at which the tension of the vapour is greater than the tension of dissociation of the hydrated salt, the hydrated oxalate is formed. 4. No rise in temperature takes place when chloral vapour and steam are brought together. W. C. W.

**Heat of Formation of Chloral Hydrate.** By BERTHELOT (*Compt. rend.*, 89, 1099—1102).—The author denies that the experiments of Wurtz were sufficiently delicate to prove that no heat is evolved when the vapours of chloral and water are brought together. W. C. W.

**Heat of Formation of Chloral Hydrate.** By A. WURTZ (*Compt. rend.*, 90, 24, 25).—A reply to the criticisms of Berthelot. W. C. W.

**Relations between the Physical Properties of Organic Bodies and their Chemical Constitution.** By J. W. BRÜHL (*Ber.*, 12, 2135—2148).—Gladstone and Dale, as well as others, have



shown that the fraction  $\frac{n-1}{d}$  (where  $n$  stands for the index of refraction, and  $d$  for the density of the body) gives a numerical value which is independent of the temperature. This number may be called the specific refractive index. In the case of bodies of small refractive power,  $n$  may be replaced by the refractive index of any wave-length (colour), but when the body has strongly refractive properties, dispersion interferes. If, however,  $\mu_{\lambda_1}$  be called the observed index of the wave-length,  $\lambda_1$  and  $\mu_{\lambda_2}$  that of wave-length  $\lambda_2$ , then as  $\mu_{\lambda_1} = A + \frac{B}{\lambda_1^2}$  and  $\mu_{\lambda_2} = A + \frac{B}{\lambda_2^2}$ ,  $B = \frac{\mu_{\lambda_2} - \mu_{\lambda_1}}{\frac{1}{\lambda_2^2} - \frac{1}{\lambda_1^2}}$  and  $A = \mu_{\lambda_1} - \frac{B}{\lambda_1^2}$  where  $B$  is the coefficient of dispersion, and  $A$  the required index for a beam of infinite wave-length. This value of  $A$  can now be introduced into the formula  $\frac{n-1}{d}$ , instead of  $n$ , as the true coefficient of refraction, independent of dispersion. For every substance, therefore,  $\frac{A-1}{d}$  is a constant which is influenced only by the chemical nature of the substance. If this constant be multiplied by the molecular weight  $P$  of any body, then  $P \cdot \frac{A-1}{d}$ , referred to chemically comparable quantities, is the molecular refractive index, called in the rest of this paper the molecular refraction of the body.

Landolt has shown that the atoms of all compounds maintain their own refractive index, independently of the manner in which they are grouped; and Gladstone has also shown that the molecular refractive power of compounds is the sum of the refraction of the atoms. Many exceptions, however, were found to this law, such as benzene-derivatives, terpenes, many alkaloids, ethereal oils, and other compounds rich in carbon. The molecular refraction of these bodies is greater than that calculated from the sum of atomic refraction. The author has, however, succeeded in discovering an interdependence between the composition and optical relations of these bodies; that in unsaturated bodies atoms which are more than once directly combined with each other possess a more active influence in the propagation of light than atoms which with the same quantivalence are linked to different atoms. If, for instance, hydrogen-atoms are taken away from a saturated hydrocarbon, so that their removal induces a double combination of neighbouring carbon-atoms, the molecular refraction is greater than that calculated from the percentage composition of the body. If  $R_A$  represents the refractive equivalent of the hydrocarbon calculated from its empirical formula,  $\alpha$  the influence of a double combination upon the molecular refraction, and  $x$  the number of atoms removed, the molecular refraction of a body of the composition  $(C_nH_{m+2}) - xH_2$  is  $P \left( \frac{A-1}{d} \right) = R_A + x\alpha$ . Further, in unsaturated bodies in which there is no manifold attraction of neighbouring carbon-atoms, but where the removal of constituents of the saturated body produced a linking of carbon-atoms previously not directly combined with each

other, the constitution of the body has no particular influence on its optical properties, and its molecular refraction corresponds with its empirical composition  $P\left(\frac{A-1}{d}\right) = R_A$ . Bodies of the formula  $(C_nH_{2n+2}) - xH_2$ , in which several combinations of neighbouring carbon-atoms, and likewise attractions of non-neighbouring atoms are present, have the molecular refraction  $P\left(\frac{A-1}{d}\right) = R_A + (x-y).a$ , where  $y$  stands for the number of hydrogen-pairs whose removal produced the ring-formed linking.

Tables are appended from which the following results are obtained:—

The molecular refraction of bodies which contain one carbon-pair is greater by 2 than the value calculated from the sum of the specific atomic refraction,  $M_A = P\left(\frac{A-1}{d}\right) = R_A + 2$ . For bodies con-

taining two carbon-pairs the formula is  $M_A = P\left(\frac{A-1}{d}\right) = R_A + 4$ ;

for those containing three carbon-pairs,  $M_A = P\left(\frac{A-1}{d}\right) = R_A + 6$ .

The atomic refraction of carbon in saturated bodies is 4.86, and therefore the refraction equivalent of the group C : C is  $2 \times 4.86 + 2 = 11.72$ : hence the refraction-equivalent of the carbon-atom is  $\frac{11.72}{2} =$

5.86, and this shows that the atomic refraction of carbon is variable.

The molecular refraction of propargyl-derivatives is  $M_A = P\left(\frac{A-1}{d}\right) = R_A + 1.8$ , which would show that their constitution is  $\begin{array}{c} \text{HCH} \\ \diagup \quad \diagdown \\ \text{HC}=\text{CH} \end{array}$ , or  $\text{CH} : \text{C} - \text{CH}_3$ .

The value of the optical properties of a body in determining its chemical constitution may be seen from the following example:—

A hydrocarbon of the formula  $(C_nH_{2n+2}) - 4H$  may contain either (1) two ring-formed combinations; (2) one ring-formed and one double combination; or (3) two double combinations. Its molecular refraction would give us (1)  $M_A = R_A$ ; (2)  $M_A = R_A + 2$ ; (3)  $M_A = R_A + 4$ .  
G. T. A.

**Chemical Constitution of Organic Compounds in Relation to their Refractive Power and Density.** By J. W. BRÜHL (*Annalen*, 200, 139—231).—After referring to the researches of Gladstone and Dale (*Proc. Roy. Soc.*, 12, 448; 16, 439; and 18, 9; *Phil. Trans.*, 1858, 887; and this Journal, 3, 108; 8, 101 and 147); Landolt (*Pogg. Ann.*, 117, 368, and 123, 595); Wüllner (*ibid.*, 133, 1), and others, the author gives the details of his investigation on the specific refraction of a large number of liquid organic compounds. The refractive indices of the substances were determined for the yellow sodium line D, the red and green hydrogen lines C and F, and for the

| Name.                       | B. p.      | Sp. gr. | $\mu_D$ . | A.      | B.       | $A - \frac{1}{d}$ | Molecular refraction. | R <sub>A</sub> . | Difference between molecular refraction and R <sub>A</sub> . |
|-----------------------------|------------|---------|-----------|---------|----------|-------------------|-----------------------|------------------|--|
| Ethylene perchloride ....   | 120°       | 1.0190  | 1.50547   | 1.48431 | 0.74254  | 0.2091            | 49.66                 | 47.84            | +1.9   |
| Propyl alcohol .....        | 97         | 0.8044  | 1.38513   | 1.37542 | 0.31680  | 0.4667            | 28.00                 | 27.80            | 0.2  |
| Allyl alcohol .....         | 96.5       | 0.8510  | 1.41345   | 1.39881 | 0.50453  | 0.4670            | 27.03                 | 25.23            | 1.9  |
| Propyl aldehyde .....       | 48         | 0.8063  | 1.36366   | 1.35844 | 0.35065  | 0.4382            | 25.42                 | 25.22            | 0.2  |
| Acrolein .....              | 50         | 0.8410  | 1.39975   | 1.38010 | 0.39427  | 0.4520            | 25.31                 | 22.64            | 2.7  |
| Propyl ethyl ether .....    | 65.3       | 0.7886  | 1.36318   | 1.35976 | 0.33768  | 0.4871            | 42.86                 | 42.67            | 0.2  |
| Allyl ethyl ether .....     | 66.5       | 0.7651  | 1.38810   | 1.37547 | 0.43882  | 0.4907            | 42.20                 | 40.10            | 2.1  |
| Propyl acetate .....        | 100        | 0.8856  | 1.38438   | 1.37427 | 0.34882  | 0.4226            | 43.11                 | 43.30            | 0.1  |
| Allyl acetate .....         | 103.5      | 0.9276  | 1.40448   | 1.39151 | 0.45468  | 0.4221            | 42.21                 | 40.42            | 1.8  |
| Isobutyric acid .....       | 153.2      | 0.9190  | 1.39300   | 1.38250 | 0.359711 | 0.4031            | 35.48                 | 35.66            | -0.1   |
| Methacrylic acid .....      | (m.p. 16°) | 0.9153  | 1.43113   | 1.41100 | 0.61013  | 0.4078            | 35.07                 | 32.98            | +2.1   |
| Amylene .....               | 35         | 0.6476  | 1.37576   | 1.36852 | 0.42173  | 0.5613            | 32.29                 | 37.20            | 2.1  |
| Valerylene .....            | 45         | 0.6786  | 1.40014   | 1.38565 | 0.51660  | 0.5683            | 38.65                 | 34.60            | 4.1  |
| Hexane .....                | 68.3       | 0.6603  | 1.37536   | 1.36538 | 0.34162  | 0.5534            | 47.59                 | 47.22            | 0.1  |
| Diallyl .....               | 50.8       | 0.6850  | 1.40102   | 1.38589 | 0.52733  | 0.5609            | 45.99                 | 42.06            | 3.9  |
| Benzene .....               | 79.3       | 0.8759  | 1.50137   | 1.47562 | 0.90816  | 0.5414            | 42.16                 | 36.90            | 5.3  |
| Propyl chloride .....       | 44         | 0.8803  | 1.38876   | 1.37813 | 0.36474  | 0.4250            | 33.36                 | 33.14            | 0.3  |
| Allyl chloride .....        | 44.6       | 0.9379  | 1.41538   | 1.40007 | 0.53369  | 0.4266            | 32.63                 | 30.56            | 2.0  |
| Triethylamine .....         | 80.2       | 0.7277  | 1.40032   | 1.38803 | 0.43179  | 0.5332            | 53.86                 | 53.83            | 0.0  |
| Aniline .....               | 182.5      | 1.0216  | 1.58629   | 1.54741 | 1.38319  | 0.5358            | 49.83                 | 43.54            | 6.3  |
| Chlorobenzene .....         | 131.7      | 1.1066  | 1.52479   | 1.49887 | 0.32660  | 0.4504            | 50.67                 | 45.14            | 5.6  |
| Bromobenzene .....          | 154.3      | 1.4914  | 1.55977   | 1.53015 | 1.04527  | 0.3555            | 55.81                 | 50.86            | 5.4  |
| Nitrobenzene .....          | 209.1      | 1.2039  | 1.55291   | 1.51523 | 1.32400  | 0.4280            | 52.64                 | 46.76            | 5.8  |
| Toluene .....               | 110        | 0.8656  | 1.49552   | 1.47101 | 0.36692  | 0.5441            | 50.06                 | 44.34            | 5.8  |
| Orthoform .....             | 198.4      | 0.9986  | 1.57276   | 1.53716 | 1.26553  | 0.5379            | 57.66                 | 50.98            | 6.6  |
| Benzyl alcohol .....        | 205        | 1.0420  | 1.53955   | 1.51330 | 0.92458  | 0.4922            | 53.16                 | 47.24            | 6.0  |
| Mesitylene .....            | 163        | 1.8553  | 1.49116   | 1.46892 | 0.78105  | 0.5479            | 65.75                 | 59.22            | 6.6  |
| Ethyl propyl alcohol .....  | 218        | 1.0079  | 1.53695   | 1.50880 | 0.91452  | 0.5058            | 68.79                 | 62.12            | 6.7  |
| Phenyl hydrocinamate .....  | 244.8      | 1.0147  | 1.49542   | 1.47497 | 0.71305  | 0.4681            | 83.32                 | 77.32            | 6.0  |
| Propargyl alcohol .....     | 114        | 0.9715  | 0.43064   | 0.41645 | 0.49649  | 0.4237            | 24.01                 | 22.64            | 1.4  |
| Propargyl-ethyl ether ..... | 83         | 0.8326  | 0.40890   | 0.39152 | 0.43145  | 0.4702            | 39.50                 | 37.62            | 2.0  |
| Propargyl acetate .....     | 123        | 1.0052  | 0.42047   | 0.40733 | 0.45827  | 0.4052            | 39.71                 | 37.84            | 1.9  |

violet hydrogen line which occupies a position between the Fraunhofer lines F and G. These determinations were made at 20°. The specific gravities were also taken at this temperature, and referred to water at 4°. The weighings were reduced to *vacuo*.

In the table (p. 296), Column IV gives the index of refraction for the sodium line; V the coefficient of refraction for a ray of infinite wave-length (consequently not influenced by dispersion) calculated by

Cauchy's formula  $\mu_\lambda = A + \frac{B}{\lambda^2}$ , in which  $\mu$  = index of refraction,

$\lambda$  the wave-length, A coefficient of refraction, and B = coefficient of dispersion. VI shows the coefficient of dispersion. VII, specific

refraction,  $\frac{A-1}{d}$ . VIII, molecular refraction; and IX, the molecular

refraction  $R_A$ , calculated from the following atomic refractions:—C 4.86, H 1.29, O 2.9, Cl 9.53, Br 14.75, and N 5.35.

The following conclusions amongst others were deduced from a consideration of the above data:—1. When an organic body loses 2 atoms of hydrogen, forming a compound in which two of the carbon-atoms are united together by a double affinity, the specific gravity is increased by 0.04 (*circa*), the coefficient of refraction by 0.02, and the coefficient of dispersion is also larger. 2. The atomic refraction of monad elements is constant.

W. C. W.

## Inorganic Chemistry.

**Preparation of Hydroxylamine.** By G. BERTONI (*Gazzetta*, 9, 569—570).—In order to avoid the inconveniences attending the precipitation of the tin by hydrogen sulphide and the evaporation of large quantities of solution containing free hydrochloric acid, as in the usual method of preparing hydroxylamine hydrochloride, the author employs lead oxide to precipitate the tin and hydrochloric acid; it has moreover the additional advantage of entirely removing the iron chloride which is always present and causes the decomposition of a large proportion of the hydroxylamine salt during the evaporation. The product of the reaction of the tin and hydrochloric acid on the nitrate is poured into a large basin, and hydrated lead oxide or carbonate added in successive portions until there is a slight excess with respect to the tin originally employed in the reduction: when the precipitation is completed, which happens in the course of a few days, the liquid is neutral or slightly alkaline, and after removal of the lead by sulphuric acid, should give no precipitate of tin sulphide with sulphuretted hydrogen. The liquid is then decanted, the residue heated several times with water to dissolve out the hydroxylamine salt, and the small quantity of lead which is present is precipitated by hydrogen sulphide. After filtration and evaporation to dryness, the hydroxylamine salt is extracted from the residue in the manner described by Lossen.

C. E. G.

**Conversion of Hydroxylamine into Nitrous and Nitric Acids.**

By G. BEERONI (*Gazzetta*, 9, 571—574).—When a dilute solution of hydroxylamine is rendered alkaline with baryta and treated with potassium permanganate, it is immediately reduced, and on examining the solution it will be found to contain nitrous acid. If the hydroxylamine solution is rendered acid with sulphuric acid, its reducing action on the permanganate is very much slower, and in this case nitric acid is formed. In neither reaction, however, is the whole of the hydroxylamine converted into the acid. Chromic acid behaves in a somewhat similar manner, producing nitric and nitrous acids, whilst the oxides of the noble metals yield nitrous acid only. The author hopes to found a quantitative process for the estimation of hydroxylamine on this reaction. Red blood-corpuscles are deoxidised by hydroxylamine, but the products formed have not been examined. The powerful reducing action of hydroxylamine causes it to act as an energetic poison when injected subcutaneously, and also when exhibited internally.

C. E. G.

**Reduction of Carbonic Anhydride by Phosphorus at Ordinary Temperatures.** By A. R. LEEDS (*Ber.*, 12, 2131).—The author finds that, although large quantities of phosphine are produced under the conditions stated in a previous paper (this vol. 237), no reduction of carbonic anhydride to carbonic oxide takes place.

G. T. A.

**A New Hydride of Silicon.** By J. OGIER (*Compt. rend.*, 89, 1068—1070).—Silicon tetrahydride is decomposed by the electric discharge, hydrogen being liberated, and a yellow deposit formed which has the composition  $\text{SiH}_2$ . The new compound ignites on percussion, and burns when heated in the air: it also takes fire in an atmosphere of chlorine.

When exposed to a temperature of  $400^\circ$ , the tetrahydride splits up into hydrogen and silicon.

Phosphoretted and arseniuretted hydrogen are also decomposed by the electric discharge, with formation of solid hydrides.

W. C. W.

**Luminosity of Phosphorus.** By W. MÜLLER-ERZBACH (*Ber.*, 12, 2130).—The statement of Joubert (*Compt. rend.*, 79, 693) that the luminosity of phosphorus is due to oxidation of its vapour is not new. The author has stated the same fact in *Pogg. Ann.*, 141, 95, and *Ber.*, 3, 84.

G. T. A.

**Pentathionic Acid.** By F. KESSLER (*Annalen*, 200, 256—259).—In replying to Spring's paper on the non-existence of pentathionic acid (*Ann.*, 199, 79) the author points out that his analyses (*Pogg. Ann.*, 74, 274) proved that the acid which is produced by the action of sulphuretted hydrogen on sulphurous acid was *penta-* and not *tetra-*thionic acid.

W. C. W.

**Reduction of Metallic Oxides by Hydrogen.** By W. MÜLLER-ERZBACH (*Ber.*, 12, 2130).—The statement made by Wright and Luff in their papers on "Researches on some Points in Chemical Dyna-

mics (this Journal, 1878, 1 and 504), that the initial temperature for the reduction of oxides depends on their physical nature, has been already published by the author (*Pogg. Ann.*, 136, 51). Also their statement that precipitated copper oxide is not reduced by hydrogen at a temperature below 83° has been forestalled by the author, who gave it as 82° (*Pogg. Ann.*, 153, 332). G. T. A.

**Copper Hydride.** By BERTHELOT (*Compt. rend.*, 89, 1005—1011).—The anomalous results observed in the amount of heat absorbed in the formation of copper hydride (which was found to vary from — 2·7 to — 8·7 in different specimens) induced the author to analyse the substance. A sample prepared by the addition of sodium hypophosphite to a solution of copper sulphate and dilute sulphuric acid, purified by washing with water containing carbonic acid, and dried on porous plates over sulphuric acid in an atmosphere of carbonic anhydride, had the following composition:

Cu 87·2 H; 0·08; H<sub>2</sub>O 1·3; S 0·28; P 1·34; O combined with Cu 4·6. O combined with S and P, loss, &c., 5·2 per cent.

It may be regarded as a complex compound of hydroxide and phosphate of copper.

When boiled in water, the so-called hydride gives off hydrogen, and leaves a residue which contains besides copper, small quantities of oxygen, sulphur, and phosphorus. W. C. W.

**Copper Hydride.** By A. WURTZ (*Compt. rend.*, 89, 1066—1068).—In reply to Berthelot's criticisms, the author points out that pure cuprous hydride can be obtained by the electrolytic decomposition of a dilute solution of copper sulphate, or by the action of sodium hypophosphite, Na<sub>2</sub>SO<sub>2</sub>, on copper sulphate. When the hydride is treated with hydrochloric acid, the volume of hydrogen liberated is twice that set free when the hydride is decomposed by heat. W. C. W.

**Copper Hydride. A Reply to Wurtz.** By BERTHELOT (*Compt. rend.*, 89, 1097—1099).—The author maintains that the existence of cuprous hydride is purely hypothetical, since the so-called compound invariably contains constitutional water. W. C. W.

**Copper Hydride.** By A. WURTZ (*Compt. rend.*, 90, 22—24).—In the preparation of cuprous hydride at the ordinary temperature, the portion which is first deposited contains only very slight traces of phosphate. The mean of two analyses gave—

|                       | Found. | Calculated. |
|-----------------------|--------|-------------|
| Cu <sub>2</sub> ..... | 98·52  | 98·45       |
| H <sub>2</sub> .....  | 1·48   | 1·55        |

W. C. W.

**Atomic Weight of Antimony.** By F. KESSELER (*J. pr. Chem.* [2], 20, 114—123).—(Comp. this Jour., 36, 772.) A critical discussion of the methods and results of the five more important investigations of this constant, leads the author to the following conclusions:—The determinations of Schneider, by the ignition of a native sulphide

(Arnsberg glance), in hydrogen gas, are untrustworthy, he having overlooked the presence of calcspar as an impurity in the ore: so also are Cooke's numbers; both those obtained from the synthesis of  $\text{Sb}_2\text{S}_3$  in the wet way, and subsequently heating to  $210^\circ$  in a stream of hydrogen, through the oxidation of a portion of the sulphide in the latter process, due to the presence of nitrogenous impurity ( $\text{N}_2\text{O}$ ) in the hydrogen used; and also those obtained from the analyses of halogen compounds on account of the contamination of the silver precipitates with the sparingly soluble salt,  $\text{AgSbO.C}_4\text{H}_4\text{O}_6$ , and probable impurities in the  $\text{SbCl}_3(\text{H}_2\text{O})$ ,  $\text{SbBr}_3$ , and  $\text{SbI}_3(\text{SBr}_2.\text{SI}_2)$ , the two latter compounds having been prepared in presence of carbon bisulphide. On the other hand, after applying a correction to the number obtained by Dumas for the  $\text{AgSbO.C}_4\text{H}_4\text{O}_6$ , here also most probably contained in the silver precipitate, we obtain  $\text{Sb} = 122.29$ . The number assigned by Dexter, 122.33, the author regards as trustworthy, whilst the mean value obtained by the author himself from three series of experiments was 122.29. The final conclusion to be drawn is that 122.3 represents the atomic weight of the metal; or, on the assumption of Stas ( $\text{H} = 1$ ,  $\text{O} = 15.96$ ) the integral 122. C. F. C.

**Atomic Weight of Antimony.** By J. P. COOKE (*Ber.*, 12, 2123—2124).—A reply to the objections of Kessler to the author's results. (See preceding abstract, and this Journal, 36, 354 and 772.)

**Galvanic Experiments (Platinum Bases).** By E. DRECHSEL (*J. pr. Chem.* [2], 20, 378—380).—The method employed is to continuously and rapidly reverse the galvanic current from platinum poles through the solution operated upon. By acting in this manner on commercial ammonium carbonate (containing ammonium carbonate) for a period of eight hours, and then evaporating on the water-bath, a salt crystallising in fine white needles was obtained. It was found to contain 64.69 per cent. platinum, and is the salt of a platinum base; its composition could not be satisfactorily settled on account of want of material. Concentrated hydrochloric acid gives a bright green, nitric acid a sky-blue crystalline precipitate with its solution. About 0.1 gram platinum was dissolved in ten hours by the ammonium carbonate.

On working the commutator more slowly, the temperature of the liquid rises and no precipitate is formed, but by simultaneous cooling a crystalline precipitate occurs, which contains 38.6 per cent. platinum, and is also the salt of a platinum base; this yields no bright green precipitate, but an almost colourless one with hydrochloric acid, consisting of microscopic needles. By operating on a solution of glucose mixed with sodium phosphate, with very large platinum electrodes, prevented from touching each other by a sheet of filter-paper, the places on the platinum where the paper had rested were found at the end of the experiment to be covered with a brownish translucent substance, easily removable in large plates; this on ignition left a large amount of platinum, but its properties have not as yet been investigated.

H. Kolbe remarks in a note to the paper that these interesting

results have induced him to extend his earlier galvanic experiments. and to study the action of rapid change of poles on a number of salts.

F. L. T.

## Mineralogical Chemistry.

**Mineralogical Notes on the Ores of Chanarcillo, North Chili.** By A. STRENG (*Jahrb. f. Min.*, 1878, 897—927).—The specimens examined by the author were obtained from the Dolores I Mine, Chañarcillo, Atacama. The veins and deposits of the various ores of this district were described by F. A. Moesta (*Jahrb. f. Min.*, 1870, 489). According to him, the silver ores are irregularly distributed over Atacama, some occurring in the neighbourhood of the coast, and others in the Cordillera in greenstone, stratified porphyry, sedimentary and metamorphic rocks. The most considerable deposits of ore occur in the stratified formations of Chañarcillo, in limestone of the Upper Jura formation, in which there are vertical veins and intrusive layers of eruptive rocks. There are numerous veins of greenstone penetrating the limestone (their direction being from the south towards the north) and in these veins, where the rocks are still undecomposed, there are considerable quantities of iron-pyrites, galena and zinc-blende, all of which contain small quantities of silver, varying from four to six ounces to the centner. There are three occurrences to be taken into consideration, which are of great importance, viz.: (1) the veins; (2) the so-called "mantos;" (3) the intrusive deposits.

*The Veins.*—These consist of rich silver veins, ferruginous barren veins, and rock veins more or less of decomposed greenstone. The rock veins are undoubtedly the media through which the metalliferous deposits were brought about, as they cause an enrichment of the silver veins penetrating them.

*The Mantos.*—These are layers and zones of rock interposed with great regularity in the stratified formation; they contain silver ore, and are always metamorphosed through the action of silicates.

*The Intrusive Layers.*—These also are "mantos," consisting, however, of greenstone, and enriching the silver veins which penetrate them. The distribution of ore in the veins is very irregular, owing to the unmistakably intimate connection existing between the "manto" formation and the ore deposits, as the latter occur only where the adjacent rock (nebangestein) is "manto," or where a vein of greenstone penetrates a vein of ore. Where the adjacent rock is not "manto," the veins are filled with barren rock substance, and, speaking generally, the veins increase in richness with the depth. The silver-ores of the above locality may be divided into two large groups, viz., the uppermost, and those near the surface consisting mostly of native silver, or the compounds of silver with chlorine, bromine, iodine and mercury, whilst the lowermost deposits are either sulphides of silver or arsenical silver compounds, such as silver-glance, polybasite, proustite and pyrrargyrite.



The accompanying vein-mass can also be divided into two groups: (1) in the upper zone it consists mostly of a loam coloured yellow by ferric oxide, of a purer iron-ochre, ferruginous bitter spar, calcite, barytes and some malachite; (2) in the lower zone it is black or grey, and consists of calcite, much zinc-blende, galena, arsenic, and occasionally iron-pyrites.

It is characteristic of the deposit of silver ore that it ends at that depth or spot where the decomposition or alteration of the rock strata can no longer be detected. From these observations the author concludes that the ores in the veins are the product of the decomposition of the adjacent rock. The silver in them arises from the silver entering into the composition of the metallic sulphides distributed in the calcite and greenstone, as it appears that the richer the deposit in the veins, the poorer is the adjacent rock in iron-pyrites, galena and zinc-blende. These conclusions fully confirm the theory of Bischoff that "the metalliferous veins obtained their material from the adjacent rocks," and the recent researches of Sandberger, who proved that silver, copper, nickel and cobalt are present in many rock-forming minerals, accounting for the presence of these metals in the veins by showing conclusively that they must have been taken away from the adjacent rocks by the action of water, and deposited in the veins.

1. *Proustite*.—This mineral often occurs attached to pyrrargyrite, and is accompanied with argentite, calcite, fluor spar, iron-pyrites, feuerblende, &c., the proustite being generally completely enveloped by felt-like asbestos. Its crystals vary in size, from short crystals or fine needles to individuals 25 mm. in length, and the forms observed being the predominating scalenohedron  $R^3$ , combined with

$$\frac{1}{4}R. - \frac{1}{2}R. R. - 2R. \infty R. \infty P2. \infty P\frac{1}{2}.$$

The comparative length of the vertical axis  $c$  was found by the author to be 0.80339, and this result agrees exactly with the length of the axis  $c$ , obtained by calculation from Miller's measurements. The rhombohedron  $-2R$  occurs sometimes almost predominating, and on these crystals good measurements can be obtained. The rhombohedron  $+\frac{1}{4}R$ , occurs generally as a modification of the terminal edges of  $-\frac{1}{2}R$ , but it occurs sometimes independently. Its faces are always distinctly striated parallel to the shorter diagonal, that is, parallel to the combination-edge of  $-\frac{1}{2}R$  with  $+\frac{1}{4}R$ . This striation is caused by the alternating combination of  $\frac{1}{4}R$  and  $-\frac{1}{2}R$ . The rhombohedron  $R$  is a rare occurrence, and its faces are not generally well adapted for accurate measurements of the interfacial angles. A scalenohedron  $\frac{3}{4}R^1$ , which occurs sometimes with  $R^3$ , and the other rhombohedrons already referred to, is characterised also by a peculiar roundness and indefiniteness of its interfacial angles. This peculiarity of the interfacial angles of the two forms is confined mostly to the same portion of a crystal, whilst on other crystals nothing of the kind is observed. As a rarity there occurred a negative rhombohedron immediately beneath  $-2R$  on  $R^3$ , its combination-edges being very nearly parallel to the obtuser terminal edges of the scalenohedron: consequently it must be an obtuser rhombohedron than  $-5R$ . There were also slight indications of a rhombohedron  $\frac{1}{4}R$ . Amongst the scalenohedrons,  $R^3$  predominates,

the faces of which possess a magnificent lustre, and often exhibit a striation parallel with the combination-edge with  $\infty P2$ , this striation being caused on some individuals by the alternating combination of the scalenohedrons  $R^3$  and  $R^4$ , whilst on others it is due simply to the alternating combination of  $R^3$  and  $\infty P2$ . The scalenohedron  $R^4$  does not occur independently. The scalenohedron  $\frac{1}{2}R^4$  is a common occurrence on the obtuser terminal edges of  $R^3$ , and exhibits a striation on all its faces parallel to the combination edge with  $-\frac{1}{2}R$ , caused by the alternating combination with the latter form. The scalenohedron  $\frac{1}{3}R^2$  is a rare occurrence; it modifies the combination edges of  $R$  with  $-\frac{1}{2}R$ . On a few crystals, a scalenohedron (new to red silver ore)  $-2R\frac{1}{2}$  occurs; it combines with  $R^3$  in such a way that the combination edges with  $R^3$  are only approximately parallel to the obtuser terminal edges of that form. The faces of  $-2R\frac{1}{2}$  are horizontally striated, owing to its alternate combination with a scalenohedron  $-mR\frac{1}{2}$  (probably  $-4R\frac{1}{2}$ ). The author observed also a scalenohedron  $R\frac{1}{3}$ , occurring in alternate combination with  $\infty P2$ , and points out that Sella (*Quadro delle forme cristalline dell' Argento rosso, del Quarzo e del Calcare di Q. Sella: estratto da una memoria sulle forme cristalline dell' argento rosso letta davanti alla R. Accademia delle scienze di Torino, li 10 febbraio, 1856*) had already observed a scalenohedron  $R\frac{1}{3}$ , but Streng's measurements were of sufficient accuracy to show that his scalenohedron was really  $R\frac{1}{3}$ . The "prism zone" is very fully developed, but the individual faces are not very clearly defined, and occur in alternating combination, thus causing a very irregular, strong, vertical striation. Amongst the prisms  $\infty P2$  predominates, its faces being generally striated parallel to a prismatic edge, or else parallel to the combination-edge with  $R$ . Sometimes the latter striation is caused by the alternate combination of  $\infty P2$  with  $R^1$ , and sometimes with the scalenohedron  $R\frac{1}{3}$ . A prism  $\infty P\frac{1}{2}$  occurs tetartohedral. The prism  $\infty R$  is a rare occurrence, and is observed generally as a trigonal prism. The author could not ascertain whether proustite was hemimorphous (as might be expected with a hemihedral or tetartohedral habit of the "prism zone") owing to one end only of the crystal being developed, whilst the other end was invariably attached to the supporting surface. The basal terminal plane  $OR$  is one of the rarest occurrences on proustite crystals. Proustite crystals occur also twinned according to two laws, the first being "the twin-plane a face of  $+R$ ." The twins according to this law have their vertical axes inclined to each other at an angle of  $94^\circ 18'$ , and one individual predominates largely and forms a nucleus round which other smaller twins arrange themselves, parallel to the three directions corresponding with the three pairs of rhombohedral faces. A polysynthetical twinning was also observed occasionally, tabular crystals occurring as thin laminae being interpolated parallel to a face of  $R$ , in the principal or predominating crystal. The second twin-law is "the twin-plane a face perpendicular to the terminal edge of  $-\frac{1}{2}R$ ." The twin-axis is a terminal edge of  $-\frac{1}{2}R$ . The two crystals have a face of  $+\frac{1}{2}R$  in common, but the twin-plane is the one given above, and the vertical axes of the two crystals intersect at an angle of  $26^\circ 7'$ . A similar grouping of crystals, round a central predominating individual, was

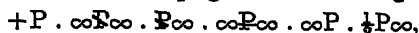
observed with twins according to the second twin-law, as was the case with those according to the first law; also for the first time, a polysynthetical twin-formation. The author considers proustite to be one of the best examples of three kinds of striation on the crystal-faces, as the latter are striated (1) through the alternate combination of two faces; (2) through the occurrence of sub-individuals; and (3) through polysynthetical twin-formation. The author appends a table of interfacial angles for all the forms observed on proustite from Chañarcillo.

2. *Pyrrargyrite*.—This mineral occurs simultaneously with proustite at Chañarcillo, the latter being generally attached to the former. The crystals of pyrrargyrite are less lustrous than those of proustite, and therefore not well adapted for accurate measurement, but the following forms were observed, viz.,  $R^3$ . —  $\frac{1}{2}R$ .  $\infty P2$  and  $\infty R$  as a trigonal prism. The terminal edges of  $-\frac{1}{2}R$  are either replaced by  $\frac{1}{4}R$ , or else by very obtuse, striated scalenohedrons, which could not be measured. The faces of  $R^3$  are strewn over with small excrescences, which aggregate into narrow swellings on the acuter edges, whilst the faces of  $\infty P2$  project so much that  $R$  occurs above it, with a re-entering angle in combination with  $R^3$ , whence it follows that the faces of  $R^3$  are sunken, as in a crystal skeleton. Some pyrrargyrite crystals are encased in a light-grey, lustreless covering, on which proustite crystals have formed. Twins occur, the twin-plane being a face of  $R$ . On analysis of a pyrrargyrite crystal, the following results were obtained, viz.:—

| Ag.   | Sb.   | As.  | S.             |
|-------|-------|------|----------------|
| 60.53 | 18.47 | 3.80 | 18.17 = 100.97 |

from which the formula  $Ag_3AsS_3 + 3Ag_3SbS_3$  is deduced. From this formula it appears that the Chañarcillo pyrrargyrite occupies an intermediate position between pyrrargyrite and proustite, as the author considered might be the case, from its occurrence simultaneously with proustite.

2. *Feuerblende*.—This mineral occurs attached to pyrrargyrite, in very small, isolated, hyacinth-red crystals, in a rhombic form resembling stilbite. The largest crystals attained a length of 1.5 mm., and a breadth of  $\frac{3}{4}$  mm. Breithaupt describes this mineral in his "Charakteristik des Mineralsystems." 3 Aufl. 1832; Phillips, in his "Elementary Introduction to Mineralogy" (Brooke and Miller); Dana, in his "System of Mineralogy," and Roemer (*Jahrb. f. Min.*, 1848, 312) are of the same opinion. Phillips gives the following forms:—



and states that  $\infty P\infty$  is striated parallel to its combination-edge with  $P\infty$ . The forms given by Dana are  $\infty P. \infty P\infty. P2. P\infty. 2P\infty$ , and he also states that  $\infty P\infty$  is striated parallel to the clinodiagonal, the cleavage-plane being also  $\infty P\infty$ . Roemer also considers the mineral to be monosymmetrical, on account of the striation being feather-like, and parallel to a terminal edge of  $P$ , whilst he was of opinion that the cleavage-plane must be a face of  $P$ .

Kenngott, however, concluded from his observations " (Uebersicht der Resultate mineralogischer Forschungen in den Jahren 1844-49,"

249), that it crystallised in the rhombic system, the forms observed being  $P \cdot \infty \bar{P}\infty \cdot \infty \bar{P}\infty$ , the cleavage direction parallel to  $\infty \bar{P}\infty$ , and the feather-like striation on  $\infty \bar{P}\infty$  was parallel to the combination edge with  $P$ . The crystals examined by Streng exhibited two types, viz., a distinctly rhombic type and a monosymmetrical type. There were three pyramids in the same zone, a prism whose obtuser edge was modified by a dull, lustreless pinacoid, and the acute edge by a pinacoid having a strong pearly lustre; no striation was observed, however, on the latter face. A dome occurred on all the pyramids. An exfoliation was observed on the crystals, parallel to the pinacoid, exhibiting a pearly lustre ( $\infty \bar{P}\infty$ ), and this exfoliation causes a striation on the other pinacoid, and also on the faces of the domes and pyramids, parallel to the combination edges with  $\infty \bar{P}\infty$ . The author concluded from the measurements obtained by him, and the results of the optical examination of the crystals, that they crystallised in the rhombic system, and did not exhibit any twin-formation. The most obtuse pyramid was chosen as primary pyramid, and the axial ratio  $a : b : c = 0.3706 : 1 : 0.1944$ .

The following table gives the various forms and the interfacial angles observed according to the authorities above named :—

| Streng.<br>(Rhombic.)           | Brooke and<br>Miller.<br>(Mono-sym-<br>metrical.) | Dana.<br>(Mono-sym-<br>metrical.) | X.          |          | Y.          | Z.      |
|---------------------------------|---|-----------------------------------|-------------|----------|-------------|---------|
|                                 |   |                                   | Calculated. | Found.   | Calculated. |         |
| $\infty \bar{P}\infty$          | $\infty \bar{R}\infty$                            | $\infty \bar{R}\infty$            | —           | —        | —           | —       |
| $\infty P\infty$                | $\infty \bar{P}\infty$                            | $\infty \bar{P}\infty$            | —           | —        | —           | —       |
| $\infty P$                      | $\infty P$  | $\infty P$                        | 40° 40'     | —        | 139° 20'    | —       |
| $P$                             | —   | —                                 | 125 32      | —        | 160 28      | 58° 30' |
| $4\bar{P}4$                     | $\frac{1}{2}\bar{R}\infty$                        | $\bar{R}\infty$                   | —           | —        | 110 52      | —       |
| $5\bar{P}5$                     | —   | —                                 | 138 46      | 137° 58' | 98 32       | 95 42   |
| $\frac{1}{2}\bar{P}\frac{1}{2}$ | $\bar{R}\infty$                                   | $2\bar{R}\infty$                  | —           | —        | 75 28       | —       |
| $\frac{1}{2}\bar{P}9$           | $P$   | $\bar{R}2(?)$                     | 150 50      | —        | 65 44       | 122 32  |
| $\bar{P}\infty$                 | —   | —                                 | 124 37½     | 124 37½  | 55 22½      | —       |

All the forms given in the first column were observed by the author, excepting  $4\bar{P}4$  and  $\frac{1}{2}\bar{P}\frac{1}{2}$ , which he converted into rhombic forms, from Brooke and Miller's measurements.\*

\* *Note by Abstractor.*—Since the above paper was written it has been shown that if the crystals be placed in the position assigned to those of rittingerite by Schrauf (viz., tabular through OP), the interfacial angles will be almost identical, and the crystal system monosymmetrical, the forms being  $OP \cdot \infty \bar{R}\infty \cdot \frac{1}{2}\bar{R}\infty \cdot P \cdot \frac{1}{2}\bar{P} \cdot \infty P \cdot \frac{1}{2}P$ . Owing, however, to the presence of sulphur in Streng's feuerblende, and its entire absence in rittingerite, it is still an open question whether the two minerals are identical. Below are given the interfacial angles of feuerblende (in Schrauf's position) compared with the interfacial angles of Schrauf's rittingerite, viz. :—

|                                 | Streng.                     | Schrauf.                  |          |
|---------------------------------|-----------------------------|---------------------------|----------|
| $\infty P - \infty P$           | $= 55^\circ 23\frac{1}{2}'$ | $55^\circ 40'$            |          |
| $P - OP$                        | $= 49^\circ 7'$             | $48^\circ 52'$            |          |
| $\frac{1}{2}\bar{P} - OP$       | $= 81^\circ$                | $81^\circ 6'$             |          |
| $\frac{1}{2}\bar{R}\infty - OP$ | $= 69^\circ 14'$            | $70^\circ 32\frac{1}{2}'$ | C. A. B. |

4. *Magnetic iron pyrites*.—Small crystals of this mineral, exhibiting the characteristic colour and forms, were observed on proustite. The forms observed were  $\infty P$ ,  $P$  and  $4P$  (the latter on a crystal from Kongsberg), and the interfacial angles coincided with those of silberkies. The author could not, however detect the slightest trace of silver in any of the crystals, although he is strongly of opinion that magnetic iron-pyrites crystallises in the rhombic system, and is isomorphous with silberkies. C. A. B.

**Water of the Ferdinandsbrunnquelle at Marienbad, Bohemia.** By W. F. GINTL (*J. pr. Chem.* [2], 20, 356—370).—The examination of this water was made in August, 1876. The spring, on August 2nd at 4.20 p. m., was yielding 1458.34 litres per hour, as the mean of three determinations. The temperature of the spring was  $10.3^{\circ}$ , the temperature of the air being  $20.2^{\circ}$ . The water was clear, colourless, and showed only a slight yellow tint in long columns. It had a feebly acid reaction, slightly sharp taste, afterwards very salt, leaving a distinctly inky after-taste. The sp. gr. of the water at  $20.6^{\circ}$  was found to be 1.0085.

Result of the analysis: 10,000 grams of water contain—

|                                    |               |
|------------------------------------|---------------|
| Potassium sulphate .....           | 0.49262 gram. |
| Sodium „ .....                     | 47.15345      |
| Calcium „ .....                    | 0.14899       |
| Sodium nitrate .....               | 0.12355       |
| Sodium chloride .....              | 17.11257      |
| Magnesium chloride .....           | 0.77146       |
| Sodium carbonate .....             | 14.54793      |
| Lithium „ .....                    | 0.19061       |
| * Ammonium „ .....                 | 0.05099       |
| Calcium „ .....                    | 4.80347       |
| Magnesium „ .....                  | 3.95385       |
| Ferrous „ .....                    | 0.53464       |
| Manganous „ .....                  | 0.13281       |
| Basic aluminium phosphate .....    | 0.06334       |
| Silicic anhydride .....            | 0.77645       |
| Organic matter .....               | 1.00521       |
| Arsenic .....                      | traces        |
| Boric anhydride .....              | traces        |
| Bromine .....                      | traces        |
| Strontium oxide .....              | traces        |
| Half-combined carbonic anhydride.. | 10.60759 „    |
| Free carbonic anhydride .....      | 31.79302 „    |

which corresponds to 16728.67 c.c. at 760 mm. b. p, and  $10.3^{\circ}$ .

The gases rising in the spring in 1000 c.c. contained—

|  |             |
|--|-------------|
| Carbonic anhydride .....                 | 938.47 c.c. |
| Oxygen .....                             | 19.17 „     |
| Nitrogen (with a trace of a hydrocarbon) | 42.46 „     |

F. L. T.

\* With traces of methylamine.

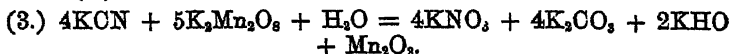
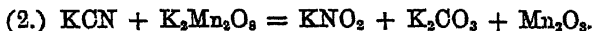
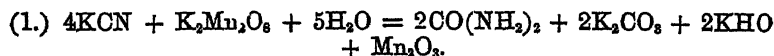
## Organic Chemistry.

**Dioxyethylmethylene.** Preparation of Methylene Chloride. By W. H. GREENE (*Compt. rend.*, **89**, 1077—1078).—*Methylene chloride*,  $\text{CH}_2\text{Cl}_2$ , is best obtained by cautiously adding hydrochloric acid to a mixture of alcohol, chloroform, and metallic zinc contained in a flask connected with a condenser. An active reaction takes place, and sufficient heat is evolved to distil over a considerable quantity of methylene chloride and chloroform. When the action ceases, more acid is added to the zinc, and the mixture is gently heated until alcohol begins to come over. On fractionating the distillate, methylene chloride (b. p.  $40-41^\circ$ ) is isolated, and the higher boiling liquid is again treated with zinc and hydrochloric acid. *Dioxyethylmethylene ether*, prepared by the action of sodium on a mixture of methylene chloride and absolute alcohol, boils at  $89^\circ$  under 769 mm. pressure, and its sp. gr. is 0.851 at  $0^\circ$ . The ether dissolves freely in alcohol and in common ether, and is somewhat soluble in water, but it separates from the aqueous solution on the addition of calcium chloride.

W. C. W.

**Action of Potassium Permanganate on Potassium Cyanide.** By E. BAUDRIMONT (*Compt. rend.*, **89**, 1115—1117).—Four equivalents of potassium cyanide are required to decolorise 5 mols. of potassium permanganate; the rate of decomposition increases with the temperature and with the strength of the solutions, but it is diminished by strongly acidifying the mixture with sulphuric acid.

Urea, ammonia, and carbonic, nitric, nitrous, oxalic, and formic acids are the products of the decomposition. The formation of urea, nitric and nitrous acids, is represented by the following equations:—



In an alkaline solution, a considerable quantity of nitrite, and but a small quantity of urea is produced, but when the mixture is acidified with sulphuric acid, the yield of urea is greatly increased.

W. C. W.

**Cyanamide.** By E. DRECHSEL (*J. pr. Chem.* [2], **20**, 77—97).—The author gives, in the first instance, details of improved methods for the preparation of cyanamide, both from potassium cyanate and from ammonium thiocyanate. Volhard's method of preparation from the latter salt, viz., conversion into thiocarbamide and treatment of this compound with mercuric oxide, is supplemented by treatment of the residues from the first of these processes, thus:—A crude melam is obtained by heating until the mass becomes solid; it is then finely powdered and heated with an equal weight of quick-lime; the resulting cyanamide is isolated by the ordinary treatment. By the method

thus completed the author obtained from 4.5 kilos. ammonium thiocyanate, 1010 grams thiocarbamide (yielding about 400 grams cyanamide), and from the 727 grams melam obtained from the residues, 292 grams cyanamide; the total yield of cyanamide being thus 15 per cent. of the salt employed.

Bodies of the formula  $n(\text{CN.NH}_2)$ , are converted into cyanamide by similar treatment, probably yielding in the first instance melam (the formation of ammonia accompanied by evolution of heat being always observed).

The formation of calcium cyanide from melam and lime may be represented by the equation—

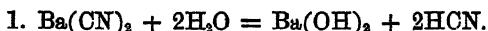


or as occurring in the following stages:—

- I.  $\text{C}_6\text{H}_9\text{N}_{11} + 4\text{CaO} = 2\text{Ca}(\text{OCN})_2 + 3\text{NH}_3 + (2\text{Ca} + 2\text{CN} + \text{N}_2).$
- II.  $2\text{Ca}(\text{OCN})_2 = 2\text{CaCN}_2 + 2\text{CO}_2.$
- III.  $\begin{cases} (a) 2\text{Ca} + 2\text{CN} + \text{N}_2 = 2\text{CaCN}_2, \text{ or} \\ (b) \text{Ca}(\text{CN})_2 + \text{Ca} + \text{N}_2 = 2\text{CaCN}_2. \end{cases}$

The last of these equations was verified (so far as the analogy holds good) by passing the vapours of sodium over potassium cyanide kept at a red heat in an atmosphere of nitrogen, when a cyanide was formed, thus:  $\text{KCN} + \text{N} + \text{Na} = \text{KNaCN}_2$ . The conversion of barium cyanide into cyanide, and the possibility of the direct removal of the carbon-atom, by which the formula of the first differs from that of the latter, were investigated by the following experiment:—Pure barium ferrocyanide was heated to redness in an atmosphere of nitrogen or hydrogen; cyanamide was identified amongst the products of the reaction. The direct observation with barium cyanide was beset with the difficulty of obtaining it. Two methods of preparation were attempted: first, dry hydrocyanic acid was passed into a solution of barium oxide in anhydrous methyl alcohol, the reaction taking place in an atmosphere of hydrogen. The product, however, was a methoxycyanide, crystallising with 1 mol. of the alcohol in white shining plates  $\text{Ba}(\text{OMe})\text{CN} + \text{MeOH}$ ; on heating, it was resolved according to the equation:  $2\text{Ba}(\text{OMe})\text{CN} = \text{CNBa.O.BaCN} + \text{Me}_2\text{O}$ . The oxycyanide, heated in an atmosphere of nitrogen, yielded cyanamide. Secondly, cyanogen gas was passed over heated barium-amalgam, air being previously expelled by a stream of hydrogen. In this case also cyanamide was formed. The conversion of barium cyanide into cyanide is thus established: the non-formation of cyanogen, when the compounds investigated were heated in an atmosphere of nitrogen; and of acetylene when hydrogen was employed, negatives the hypothesis of the direct removal of a carbon-atom. On the other hand, the reaction is attended with evolution of gas and formation of barium carbonate. The explanation of these phenomena, adopted by the author after a long investigation, lies in the presence of traces of moisture in the streams of nitrogen or hydrogen gas in which the substances were heated (*Dibbits, Zeits. Anal. Chem.*, 15,

121). The presence of water would probably determine the following reactions:—



In confirmation of this supposition, by analogy, the author found that on heating a mixture of potassium cyanide with potash to low redness in an atmosphere of nitrogen, a cyamide was formed, thus:  $2\text{KCN} + 4\text{KOH} = \text{K}_2\text{CN}_2 + \text{K}_2\text{CO}_3 + \text{K}_2\text{O} + \text{H}_4$ . It was also observed that on fusing together potassium cyanate and potash in a silver dish, potassium cyamide was formed, thus:

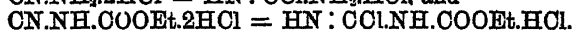


which bears on the question of the analogy of the alkali-metals to those of the alkaline earths in their relations to cyanamide.

Although the hypothesis of a direct removal of a carbon-atom from barium cyanide was rejected, the inverse problem of the addition of a carbon-atom to a cyamide appears to be solved by the observation, that on heating disodium cyamide with lamp-black, sodium cyanide is formed. The author also mentions incidentally, that on heating sodamide with carbon in a stream of hydrogen, cyanide is formed, thus:  $\text{NaH}_2\text{N} + \text{C} = \text{NaCN} + \text{H}_2$ .

*Constitution of Cyanamide.*—The view of the constitution of this body advanced by the author in a previous paper (*ibid.* [2], 11, 347), viz., that it is actually cyanamide,  $\text{CN.NH}_2$ , and not carbodiimide,  $\text{C}(\text{NH})_2$ , has been strengthened by the subsequent investigations of others, especially those of Schiff and Fileti (*Ber.*, 10, 425), and may now be regarded as established. The lengthy discussion of the value to be attached to the greater stability of the mono-, as compared with the disodium and potassium compounds of cyanamide, is concluded by assigning as the cause of the difference, the characteristics of the metals, rather than a corresponding difference of function of the two hydrogen-atoms.

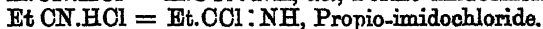
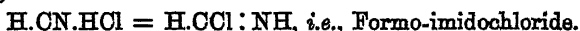
The compound of cyanamide with hydrochloric acid,  $\text{CN.NH}_2.2\text{HCl}$ , appears to contain a  $\text{CCl}$ -group, to be constituted, therefore, similarly to the imido-chlorides of Wallach (*Ber.*, 1875, 302), thus:



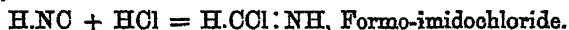
These bodies are decomposed by water, with formation of urea derivatives, the former yielding dicyanodiamidine, the latter ethyl allophanate.

The author also extends this view of the constitution of the hydrochlorides of cyanogen derivatives to the following:—

(1.) *Nitrils*—



(2.) *Carbamines*—





(3.) *Carbimides*—

$\text{CO.NH.HCl} = \text{H}_2\text{N.COCl}$ , Carbaminyll chloride.

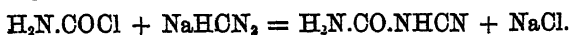
$\text{CO.NEt.HCl} = \text{EtHN.COCl}$ , Ethylcarbaminyll chloride.

(4.) *Cyanates*—

$\text{N:COEt.HCl} = \text{HN:CCl.OEt}$ , Carbamidochloride ethyl ether.

On this hypothesis, an investigation of the action of ammonia and its derivatives upon these anhydro-chlorides, would lead to interesting results, the nature of which is evident.

The action of the compounds under (3) upon sodium-cyanide should yield true cyanocarbimides, thus:—

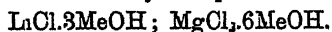


C. F. C.

**Action of Sulphuric Monochloride on Alcohols.** By P. BEHREND (*J. pr. Chem.* [2], 20, 382—384).—The author, in reply to Claesson, says that by acting on sulphuric chloride with alcohol, he obtained the body  $\text{EtO.SO}_2\text{Cl}$ ; by the action of this body, many of the alcohols may be converted into sulphates of the alcohol-radicles. Claesson did not obtain this latter result. The author complains that Claesson did not prepare the ethyl chlorosulphonate according to his (the author's) method, but prepared it by M. Müller's method, by acting with ethylene on chlorosulphonic acid. The results of Claesson differ so much from his own, that he considers there is some probability that these bodies are isomerides.

F. L. T.

**Combinations of Lithium and Magnesium Chlorides with Alcohols.** By S. E. SIMON (*J. pr. Chem.* [2], 20, 371—377).—On acting with the pure lithium and magnesium chlorides on dry ethyl and methyl alcohols, heat is evolved, and on cooling with ice or freezing mixtures, alcoholates of these chlorides crystallise out. These alcoholates are crystalline, deliquescent bodies. The formulæ representing the composition of the ethyl compounds are:  $\text{LiCl.4EtOH}$ ;  $\text{MgCl}_2.6\text{EtOH}$ , and of the methyl compounds:



F. L. T.

**Oxidation of Alcohol by an Ammoniacal Solution of Cupric Oxide.** By A. LETELLIER (*Compt. rend.*, 89, 1105).—Ethyl alcohol is oxidised to acetic acid by the action of an ammoniacal solution of copper oxide at  $180^\circ$ .

The blue colour of the ammoniacal solution is destroyed by treatment with glycerol, benzene, oil of turpentine, and by all alcohols.

W. C. W.

**Action of Diastase on Starch-paste.** By A. HERZFELD (*Ber.*, 12, 2120—2123).—The final products of the action of diastase on starch are maltose and achroodextrin. As regards the preparation of maltose, it is found that crystallisation takes place much more readily when the solution in hot alcohol of 80—85 per cent. is left standing in the cold for some time in a closed vessel before the alcohol is evaporated.

Above a temperature of  $65^{\circ}$ , besides maltose, another body, soluble in diluted but not in strong alcohol, seems to be formed by the action of diastase on starch. It forms a slightly coloured uncrystallisable gummy mass, very soluble in water. It has a faint sweet taste, which may be due to its conversion by the saliva into sugar. It is evidently identical with Bondonneau's  $\gamma$ -dextrin, but the author prefers to call it maltodextrin. It has about one-third the reducing power of maltose on Fehling's solution. Its acetyl compound differs from those of erythro- and achroo-dextrin, in that when considerable quantities of it are dissolved in hot alcohol, none of it separates out.

The author has also formed acetyl-compounds with cane- and milk-sugar, maltose, and dextrose, which he is further investigating.

G. T. A.

**Spontaneous Decomposition of Dichlorethylamine.** By J. TSCHERNIAK (*Ber.*, 12, 2129—2130).—Dichlorethylamine can be kept for a long time unchanged if it is perfectly pure, or if it is covered by a layer of water.

G. T. A.

**Desulphuration of Guanidine Thiocyanate.** By S. BYK (*J. pr. Chem.* [2], 20, 328—351).—Attempts were made to obtain cyanoguanidine from guanidine thiocyanate by the desulphurising action of the oxides of mercury and lead, but without success. Guanidine thiocyanate cannot be desulphurised in alcoholic or aqueous solutions by mercuric or plumbic oxides; mercuric oxide in aqueous solutions produces a compound  $(\text{CNS})_2\text{Hg}(\text{CNSH}.\text{CN}_2\text{H}_5)_2\text{HgO}$ , ammonia and carbonic anhydride being given off. On treating this compound with acetic acid, guanidine thiocyanate is formed, and also a mercuric acetothiocyanate,  $\text{Me}.\text{COOHg}.\text{CNS}$ . Hydrochloric acid produces a double salt of guanidine hydrochloride and mercuric chloride,  $\text{CN}_2\text{H}_5.\text{HCl}.\text{2HgCl}_2$ . By the action of lead on molten guanidine thiocyanate, a desulphuration occurs, no cyanoguanidine however being produced, but ammonia, hydrocyanic acid, plumbic thiocyanate, and a compound  $\text{C}_7\text{N}_{13}\text{H}_{18}\text{O}$ , termed cyanomelamidine by the author. By oxidation, it is converted into melamine, with production of hydrocyanic acid. Hydrochloric and sulphuric acids yield salts of melamine; nitric acid, by assimilation of water, gives ammeline nitrate,  $\text{C}_5\text{H}_8\text{N}_6\text{O}.\text{HNO}_3$ . Silver nitrate gives with cyanomelamidine, ammeline nitrate and ammeline-silver oxide,  $\text{C}_5\text{H}_8\text{N}_6\text{O}.\text{AgOH}$ .

F. L. T.

**Action of Ethyl Chlorocarbonate on the Amines.** By L. SCHREINER (*J. pr. Chem.* [2], 20, 124—126).—The product of the action of methylamine (aqueous) on ethyl chlorocarbonate is methyl-amidoethyl formate; it is a colourless liquid, with an ethereal smell, specifically lighter than water, and boiling at  $170^{\circ}$ . It is resolved, on boiling with potassium or barium hydrate, into alcohol, methylamine, and carbonic anhydride; the alkaline carbonates and the hydrated oxides of lead and copper are without action upon it. The following homologues were prepared:—

|                            |            |       |
|----------------------------|------------|-------|
| Methyl-amidoethyl formate, | boiling at | 170°  |
| Ethyl-                     | " "        | 175.5 |
| Propyl-                    | " "        | 186   |
| Dimethyl-                  | " "        | 139.5 |

The vapour-density of each was determined, and found to coincide with the theoretical.

It is to be observed that the above compounds are liquid at ordinary temperatures, whereas the urethanes are solid crystalline bodies. The low boiling point of the dimethyl-compound is in harmony with other cases pointed out by the author (*Annalen*, 197, 1—26).

C. F. C.

**Preparation of Glyceryl Triacetate.** By H. SCHMIDT (*Annalen*, 200, 99—101).—A good yield of triacetin is obtained by gently boiling anhydrous glycerol for 40 hours with twice its weight of glacial acetic acid in a flask provided with an upright condenser. The mixture is distilled, and the portion of the distillate boiling at 257—260° purified by solution in water and extraction with ether; 1 gram of triacetin dissolves in 5.6 c.c. of water at 27°.

W. C. W.

**Some Derivatives of Propionic Acid.** By B. FREYTAG (*J. pr. Chem.* [2], 20, 380—382).—On heating thiocarbamide and ethyl monochloropropionate in sealed tubes at 100° for 5 hours, a compound crystallises out on cooling which appears to be lactylthiocarbamide hydrochloride,  $\text{CS} \begin{matrix} \text{NH.C}_2\text{H}_5 \\ | \\ \text{NH.CO} \end{matrix} \cdot \text{HCl}$ . On repeated crystallisation

from alcohol or water it loses hydrochloric acid and is converted into lactylthiocarbamide. The aqueous solution yields a difficultly soluble crystalline platinochloride.

Thiocarbamide is dissolved by propionic anhydride at 100°, and on cooling a crystalline mass of propionyl thiocarbamide—



is obtained.

The aqueous solution has a neutral reaction, and yields a crystalline platinochloride.

On heating equal numbers of molecules of potassium thiocyanate and ethyl  $\alpha$ -monochloropropionate in tubes at 150—160° for 4—5 hours, the following reaction occurs:—



The ethyl thiocyanopropionate thus formed is decomposed on distillation, but may be purified by distillation in a current of steam. The amyl thiocyanopropionate is obtained in a similar manner.

Further experiments have been commenced with the diethyl ketone obtained from calcium propionate; an oxycaproic acid is obtained by the action of hydrocyanic and hydrochloric acids, which the author intends comparing with the one obtained by Frankland and Duppa.

F. L. T.

**Nitrils from Hydrocyanic Acid and Acetaldehydeammonia.** By S. C. PASSAVANT (*Annalen*, 200, 120—138).—When a solution of aldehydeammonia in 30 per cent. hydrocyanic acid is acidified with dilute sulphuric acid,  $\alpha$ -amidopropionitril immediately separates out as a colourless unstable oil. In the course of a few days needle-shaped crystals of imidopropionitril are deposited, and if the mixture is frequently shaken and is exposed to diffused sunlight for four or five weeks hydrocyanaldine and parahydrocyanaldine crystallise out.

$\alpha$ -Imidopropionitril forms glistening colourless needle-shaped crystals which dissolve in ether and alcohol, and also, although less freely, in water. The acid melts at  $68^\circ$ , and sublimes when cautiously heated. The aqueous solution is not precipitated by silver nitrate at the ordinary temperature, but on heating the mixture silver cyanide is thrown down. The hydrochloride,  $C_3H_5N_3 \cdot HCl$ , obtained by passing dry hydrochloric acid gas into an ethereal solution of imidopropionitril is a white crystalline powder, soluble in absolute alcohol, insoluble in absolute ether, and decomposed by water.

$\alpha$ -Imidopropionic or diethylidenelactamic acid—



isomeric with the ethylenedilactamic acid of Heintz (*ibid.*, 152, 42) is prepared by decomposing with dilute sulphuric acid the barium salt which is formed by boiling  $\alpha$ -imidopropionitril with baryta-water. The barium salt and the free acid are hygroscopic amorphous powders, insoluble in alcohol. The nitril, when treated with sodium nitrite and nitric acid, yields a nitroso-compound in the form of a pale-yellow oil which is heavier than water and is soluble in alcohol and ether. It is decomposed by heat, with evolution of nitrous fumes, aldehyde, and hydrocyanic acid.

**Hydrocyanaldine**, described by Strecker (*ibid.*, 91, 349), melts at  $115^\circ$  and sublimes when cautiously heated. It is freely soluble in glycerol, in acetone, and in hot alcohol and hot acetic acid. It is deposited in triclinic prisms from an ethereal solution containing imido-propionitril. It is the nitril of triethylidenelactamic acid or nitrilopropionitril,  $N(CHMe.CN)_3$ , and can be prepared by adding hydrochloric acid to a mixture of amido- and imido-propionitril in their molecular proportions. If the liquid is warmed, *parahydrocyanaldine* is also formed. This body crystallises in the rhombic system and is sparingly soluble in absolute alcohol, water, and glycerol, but dissolves freely in acetone. It melts at  $232^\circ$  and sublimes when cautiously heated. It resembles hydrocyanaldine in its behaviour with silver nitrate and with potash.

Attempts to prepare Strecker's base,  $C_3H_{15}N_3$  (*ibid.*, 130, 122), by the action of hydrocyanic acid on aldehyde-ammonia were unsuccessful. W. C. W.

**Synthesis of Normal Nonoic Acid and of an Isomeride of Palmitic Acid.** By F. JOURDAN.—*Ethyllic heptylacetoacetate*,  $Me.CO.CH(C_7H_{15}).COOEt$ , is formed by heating to  $100^\circ$  the theoretical quantities of ethylic acetoacetate, normal heptyl iodide, and an

alcoholic solution (8 per cent) of sodium ethylate. When the reaction is completed, the alcohol is distilled off and water added to the residue. The lighter layer of liquid is dried over potassium carbonate and fractionated. The pure ethereal salt is a colourless, oily liquid, b. p. 271—273° (uncorr.), sp. gr. 0.9324 at 17.7°. By the action of alcoholic potash it yields methyloctyl ketone,  $\text{Me.CO.CH}_2\text{C}_7\text{H}_{15}$ , and potassium acetate and heptylacetate. The ketone is a clear mobile liquid, not miscible with water, boils at 214°, and solidifies to a crystalline mass when cooled in a freezing mixture. Its sp. gr. at 17.7° is 0.8294.

A concentrated aqueous solution of potash decomposes ethylic heptylacetate, forming acetic and heptylacetic acids and a small quantity of methyloctyl ketone. Heptylacetic acid melts at 12°, boils at 253°, and is identical with the nonoic acid of Zincke and Franchimont (*Annalen*, 164, 335; this Journal, 1872, 300).

*Ethylic diheptylacetate*,  $\text{Me.CO.C(C}_7\text{H}_{15})_2\text{COOEt}$ , is prepared by boiling for two days in a flask, provided with an upright condenser, a solution of sodium ethylate in absolute alcohol, ethylic heptylacetate, and normal heptyl iodide. To prevent moisture being absorbed during the operation, the open end of the condenser is connected with a drying tube containing solid potash. After distilling off the alcohol and adding water to the residue, an oily liquid is obtained which contains heptyl iodide, methyloctyl ketone, ethylic heptylacetate, ethylic diheptylacetate,  $\text{CH(C}_7\text{H}_{15})_2\text{COOEt}$  (b. p. 308.5—311°), and ethylic diheptylacetate,  $\text{Me.CO.C(C}_7\text{H}_{15})_2\text{COOEt}$ . These bodies were separated by fractional distillation. Ethylic diheptylacetate is an oily liquid, sp. gr. 0.8907 at 17.5°, b. p. 331—335°. When boiled with a 20 per cent. aqueous solution of potash, it splits up into carbonic anhydride and methyl diheptylcarbinketone,  $\text{Me.CO.CH(C}_7\text{H}_{15})_2$ , a colourless liquid, sp. gr. 0.826 at 17°, boiling at 300—304°.

A concentrated solution of potash decomposes the ethereal salt with formation of ethyl alcohol and acetic and diheptylacetic acids.

*Diheptylacetic acid*,  $\text{CH(C}_7\text{H}_{15})_2\text{COOH}$ , melts at 27°, and boils between 240° and 250° under 80—90 mm. pressure. It dissolves freely in alcohol, ether, and benzene, but is insoluble in water. *Copper diheptylacetate*,  $\text{Cu(C}_{16}\text{H}_{31}\text{O}_2)_2$ , is deposited from an alcoholic solution as a granular crystalline mass (m. p. 227°). It is the only salt of this acid which has characteristic properties. W. C. W.

**Hydroxyvaleric Acids and Angelic Acids.** By W. v. MILLER (*Annalen*, 200, 261—285).—The oxidation of valeric acid (prepared from isobutyl carbinol) by potassium permanganate was investigated some time since by Neubauer, and stated by him to yield Büchner's angelic acid (*Annalen*, 106, 62; 42, 226). The author, doubting Neubauer's results, has repeated the investigation. On distillation with dilute sulphuric acid, the mixed products of oxidation yielded a volatile acid (m. p. 69.5°), crystallising in prisms of the monosymmetric system ( $a : b : c = 1.535 : 1 : 0.706$ ;  $\beta = 74.13^\circ$ ), and having the composition of an angelic acid; the barium salt crystallised in needles containing 2 mols.  $\text{H}_2\text{O}$ . The observed melting point of the

acid differs widely from that of Büchner's isomeride ( $45^{\circ}$ ). It also lies above that of methylcrotonic acid ( $62.5^{\circ}$ —Frankland and Duppa), but the difference is not sufficient to exclude the probability of identity. To solve this point, the latter acid was prepared by Frankland's method (*Ann.*, 136, 36) and by Rohrbeck's (*ibid.*, 188, 229); the products were identical; the acid was found to crystallise in plates (m. p.  $65^{\circ}$ ), belonging to the asymmetrical system, and yielded a barium salt crystallising with 4 mols.  $H_2O$ . The acid in question was therefore investigated as a new isomeride. The valeric acid studied by Neubauer being a mixture of ethylmethylacetic acid and isobutylformic acid, these acids were prepared by synthetic methods and severally oxidised by permanganate. From the latter an acid was obtained identical in properties with that under discussion.

A further examination of the products of oxidation of the original valeric acids showed that a hydroxy-acid was also present; this was isolated in the crystalline form (m. p.  $63^{\circ}$ ) and found to be identical with that obtained by Saytzeff (*ibid.*, 197, 72) by the action of phosphorus trichloride on ethylic  $\beta$ -hydroxyisobutyl formate. It would seem, therefore, that the isomeride in question is dimethylacrylic acid,  $Me_2C : CH.COOH$ , and that it is formed through the medium of  $\beta$ -hydroxyisobutyl formic acid,  $Me_2C(OH).CH_2.COOH$ . The formation of isobutyric acid, which is stated by Neubauer to accompany that of angelic acid, is also denied by the author on the grounds of his experimental results.

The oxidation of the second constituent of ordinary valeric acid, viz., ethylmethylacetic acid, was next investigated. The acid was prepared by the synthetic method of Saur (*ibid.*, 188, 259), and oxidised in dilute alkaline solution by permanganate. The mixed product was treated by the distillation method, as well as by exhaustion with ether, and in both cases a crystalline acid was obtained (m. p.  $68^{\circ}$ ), which was identified as  $\alpha$ -hydroxyethylmethylacetic acid; the absence of methylcrotonic acid was also established. This hydroxy-acid, therefore, does not yield the corresponding angelic acid on distillation with sulphuric acid, and differs in this respect from the previous isomeride. The conversion is brought about, however, by the prolonged action of sulphuric acid at  $115$ — $130^{\circ}$ .

C. F. C.

**Pyroterebic Acid.** By J. BREDT and R. FITTIG (*Annalen*, 200, 259, 260).—The liquid which is produced by the destructive distillation of terebic acid is a mixture of lactone and pyroterebic acid.

W. C. W.

**Action of Methyl Iodide on Asparagine.** By P. GRIESS (*Ber.*, 12, 2117—2119).—In endeavouring to introduce methyl into asparagine in place of hydrogen by the action of methyl iodide (and methyl alcohol) on a solution of this body in potash, a new acid was obtained in addition to tetramethylammonium iodide. This acid,  $C_4H_8NO_2$ , is tolerably soluble in hot water, but less readily in alcohol, and is almost insoluble in ether. It has a strongly acid taste; and when heated, first melts and then blackens with evolution of pungent vapours.

If the constitution of this body is rightly expressed by the formula,

$\text{COOH.C}_2\text{H}_5\text{—}\diagup\text{CO}\diagdown\text{NH}$ , it bears the same relation to aspartic acid that lactimide does to alanine.

The barium salt,  $(\text{C}_4\text{H}_4\text{NO}_3)_2\text{Ba} + 6\text{H}_2\text{O}$ , forms white foliated soluble crystals. The neutral silver salt,  $\text{C}_4\text{H}_4\text{NO}_3\text{Ag}$ , is obtained in the form of minute needles or plates when a neutral solution of the ammonium salt is decomposed by silver nitrate. When this salt is dissolved in hot water, a basic silver salt,  $\text{C}_4\text{H}_3\text{NO}_3\text{Ag}_2$ , separates out on cooling. It is also obtained, but in an amorphous state, when silver nitrate is added to a solution of the acid in excess of dilute ammonia.

G. T. A.

**Preparation of Bromobenzene and Iodobenzene.** By W. H. GREENE (*Compt. rend.*, 90, 40—41).—The best method of preparing moniodobenzene, is to allow chloride of iodine to drop slowly into benzene containing a small quantity of aluminium chloride. To avoid the formation of higher iodides, a large excess of benzene should be used.

Mono- and dibromo-benzene are easily obtained by warming a mixture of benzene and bromine with some aluminium chloride in a flask connected with an upright condenser.

W. C. W.

**Action of Cyanogen Compounds on Diazobenzene.** By P. GRIESS (*Ber.*, 12, 2119—2120).—The author has obtained a compound of diazobenzene with hydroferricyanic acid and another with hydronitroprussic acid. The first consists of  $(\text{C}_6\text{H}_4\text{N}_2)_2\text{H}_2(\text{Fe}_2\text{C}_2\text{N}_4)$ , the second of  $(\text{C}_6\text{H}_4\text{N}_2)_2\text{H}_2(\text{FeC}_2\text{N}_3\text{NO}) + \text{H}_2\text{O}$ .

They both crystallise well, and are tolerably stable. Diazobenzene and similar bodies also yield with potassium permanganate salt-like compounds which have remarkably explosive properties. Similar compounds have been obtained by Gabriel (*Ber.*, 9, 132, and 12, 1637).

G. T. A.

**Ethylene Derivatives of Phenol and Salicylic Acid.** By A. WEDDIGE (*J. pr. Chem.* [2], 20, 127—128).—Ethylenediparanitrophenol,  $\text{C}_6\text{H}_4(\text{O.C}_6\text{H}_4\text{NO}_2)_2$ , formed on heating ethylene bromide with the sodium derivative of paranitrophenol, crystallises from its alcoholic solution in small needles (m. p.  $143^\circ$ ), but is insoluble in water. On treatment with tin and hydrochloric acid, it yields a base which crystallises from its alcoholic solution in reddish needles. In the first-named reaction there is formed in addition, a body which appears to be bromethylparanitrophenol,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{O.C}_2\text{H}_4\text{Br}$ ; it crystallises in large yellowish tables (m. p.  $62\text{—}63^\circ$ ), and reacts with paranitrophenol sodium in alcoholic solution to form ethylenediparanitrophenol.

The corresponding ortho-compounds were prepared by the analogous reaction. The nitro-compound melts at  $162\text{—}163^\circ$ , and yields a crystalline base (m. p.  $127^\circ$ ) on reduction. The bromethylorthonitrophenol is a crystalline body which melts at  $38\text{—}40^\circ$ , and remains in the molten state for some time after cooling.

Diethyl ethylenesalicylate,  $\text{C}_6\text{H}_4(\text{O.C}_2\text{H}_4\text{COOEt})_2$ , is formed by heating sodium ethylsalicylate with ethylene bromide at  $120\text{—}130^\circ$ . It

crystallises from alcoholic solution in thick plates (m. p. 96—97°). On saponification with alcoholic potash, it yields *ethylenedisalicylic acid*,  $C_2H_4(O.C_6H_4.COOH)_2$ , which crystallises from a hot saturated aqueous solution in long silky needles (m. p. 151—152°).

The author is engaged in completing and generalising his results, of which this is a preliminary communication. C. F. C.

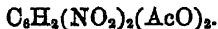
**Quinic Acid, Quinone and Allied Compounds.** By O. HESSE (*Annalen*, 200, 232—255).—*Tetrucetylquinide*,  $C_7H_5Ac_4O_5$ , obtained by the action of acetic anhydride on quinic acid at 170°, is a vitreous amorphous mass insoluble in cold water. It is deposited from a solution in boiling alcohol, in which it is sparingly soluble, in granular crystals (m. p. 124°). The compound melts in boiling water, undergoing slight decomposition. When bromine acts on an aqueous solution of quinic acid, protocatechuic and a brominated acid are formed. These acids are easily separated by the greater solubility of the protocatechuic acid in hot water. The new acid crystallises in colourless needles and plates, which are insoluble in cold water, but dissolve freely in ether. Quinic acid dissolves in hot hydrochloric acid, and the solution when heated at 150° decomposes with formation of quinol and parahydroxybenzoic acid. Protocatechuic acid is produced when quinic acid is fused with potash or soda.

Quinone can be readily purified by recrystallisation from ligroin or light petroleum, when it is obtained in beautiful yellow prisms. The author states, in contradiction to Sarauw (*Ber.*, 12, 680) that this body is not converted into an acetyl-derivative by the action of acetic anhydride.

He regards it as the aldehyde of the unknown quinonic acid,  $C_6H_4O_4$ .

*Quinol* melts at 168—169° (uncorr.), and begins to sublime at 158°. When a very narrow tube is used in the determination of the melting point, a portion of the quinol decomposes.

*Diacetylquinol* prepared by Radkowski (*N. Handwort f. Chem.*, 2, 560) by warming a mixture of acetic anhydride and quinol, crystallises in colourless plates (m. p. 121°), which are soluble in benzene, ether, chloroform, hot alcohol, and in boiling acetic acid. It is not acted on by ferric chloride or by silver nitrate, but by the action of strong nitric acid it is converted into *dinitrodiacetylquinol*,



This compound crystallises in yellow plates (m. p. 94°), which dissolve freely in chloroform, ether, and alcohol. The crystals are soluble in ammonia, soda, and milk of lime, forming yellow liquids.

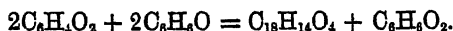
*Dipropionylquinol* is obtained in colourless crystalline plates (m. p. 113°) by heating a mixture of propionic anhydride and quinol at 150°. It dissolves in chloroform, ether, and acetone. *Mononitrodipropionylquinol*,  $C_6H_3(NO_2)(C_2H_5O)_3$ , prepared by treating the preceding compound with strong nitric acid, crystallises in pale-yellow plates (m. p. 86°) soluble in chloroform, ether, alcohol, and hot water. With soda, it produces a blue coloration, and with ammonia a brown colour, changing to purple and blue.



**Quinhydrone.**—When this compound is treated with acetic anhydride it splits up into equal molecules of quinone and diacetylquinol. This reaction confirms the accuracy of Graebe's (*Ann.*, 146, 36) formula,  $C_6H_4(OH).O.O.(OH)C_6H_4$ , for quinhydrone.

**Phenoquinone** may be prepared by adding a hot solution of phenol to quinone dissolved in boiling petroleum ether, and is deposited in red needle-shaped crystals when the mixture cools. Neither quinhydrone nor quinol is formed, and no hydrogen is evolved in the reaction.

$C_6H_4O_2 + 2C_6H_5O = C_6H_4O_2.2C_6H_5O$ . According to Wichelhaus the following equation represents the formation of phenoquinone—



The author also disputes the correctness of the formula  $C_{20}H_{18}O_6$ , assigned by Wichelhaus (*Ber.*, 12, 1500) to methylquinhydrone, since his analytical results and the reaction which takes place in preparing the compound, both indicate  $C_{20}H_{20}O_6$  as the true composition of methylquinhydrone.

W. C. W.

**Action of Acetic Anhydride on Phenolic Aldehydes.** By P. BARBIER (*Compt. rend.*, 90, 37—39).—When a mixture of two equivalents of acetic anhydride and one of salicaldehyde is heated at  $180^\circ$  for six hours, a triacetyl-derivative is formed, which on distillation splits up into acetosalicylal (b. p.  $254\text{--}256^\circ$ ) and acetic anhydride. The triacetyl compound crystallises in white needles (m. p.  $100^\circ$ ); it yields the diacetyl-derivative (m. p.  $104\text{--}105^\circ$ ) on treatment with soda. Similar compounds have been prepared from parahydroxybenzaldehyde, and from the liquid and solid hydroxytoluic aldehydes. The monacetyl-derivatives are colourless liquids boiling respectively at  $260^\circ$ ,  $267^\circ$ , and  $275^\circ$ . They all form crystalline compounds with sodium hydrogen sulphite.

W. C. W.

**Synthesis of Saligenol.** By W. H. GREENE (*Compt. rend.*, 90, 40).—Saligenol is formed when a mixture of methylene chloride (30), phenol (30), soda (40), and water (50 grams), is heated at  $100^\circ$  for six hours. The crude product is acidified with hydrochloric acid and extracted with ether. The residue which is left on evaporating the ethereal solution is treated with hot water, which dissolves out the saligenol (saligenin), leaving the greater part of the phenol undissolved. The aqueous solution is concentrated by evaporation and allowed to cool; after removing any phenol which has separated out, the liquid is left in a bell-jar over sulphuric acid until crystals of saligenol are deposited.

W. C. W.

**Phenoxyacetic Acid.** By P. FRITZSCHE (*J. pr. Chem.* [2], 20, 267—300).—The preparation of phenoxyacetic acid is described at length: sodium phenolate (10 pts.) is added to a hot concentrated solution of sodium chloracetate (12 pts.), and the whole heated with constant stirring for about an hour and a half; the product is then dissolved in water, and hydrochloric acid added, which throws down the phenoxyacetic acid as an oil, which soon solidifies. The acid

crystallises in large needles, melting at  $96^{\circ}$ , and distilling with partial decomposition at  $285^{\circ}$ . Supersaturated aqueous solutions are easily prepared.

The acid is scarcely attacked by boiling solutions of potash; it is not poisonous, and has marked antiseptic properties. Various salts are described. The potassium salt,  $\text{CH}_2(\text{OPh}).\text{COOK}$ , crystallises in brilliant scales, which may be heated to  $300^{\circ}$  without melting or decomposing. The lime salt,  $2[\text{CH}_2(\text{OPh}).\text{COO}]_2\text{Ca}.7\text{H}_2\text{O}$ , crystallises in long needles, moderately soluble in water, melting at  $120^{\circ}$ . The barium salt crystallises with 3 mols. of water. The salts of the heavy metals melt in hot water, and are therefore prepared with difficulty; none are described in detail.

Methyl and ethyl phenoxyacetate are readily prepared by heating a solution of the acid in methylic or ethylic alcohol, in a stream of hydrochloric acid; the former is an oily liquid, of somewhat pleasant odour, boiling at  $245^{\circ}$ , and having a sp. gr. of 1.15 at  $17.5^{\circ}$ ; it is insoluble in water, and mixes in all proportions with alcohol, ether, and carbon bisulphide. The ethyl salt boils at  $251^{\circ}$ , and has a sp. gr. of 1.104.

*Phenoxyacetamide*,  $\text{CH}_2(\text{OPh}).\text{CONH}_2$ , is best prepared by mixing 1 vol. of ethyl phenoxyacetate with 2 vols. of aqueous ammonia. After 3—5 days, the amide crystallises out in rhombic tables, melting at  $101.5^{\circ}$ , insoluble in cold water, slightly soluble in hot water, and easily soluble in hot alcohol. By heating the amide with phosphoric anhydride, *phenoxyacetnitril*,  $\text{CH}_2(\text{OPh}).\text{CN}$ , distils over mixed with phenol. The nitrile is an oily, colourless liquid, boiling about  $235\text{--}238^{\circ}$ , and having a sp. gr. of 1.09 at  $17.5^{\circ}$ . Hydrogen sulphide acts on this nitril with production of *phenoxyacetothiamide*,  $\text{CH}_2(\text{OPh}).\text{CSNH}_2$ , which crystallises from alcohol in rhombic prisms, difficultly soluble in water and cold alcohol; easily soluble in hot alcohol.

*Phenoxyacetanilide*,  $\text{CH}_2(\text{OPh}).\text{CONHPh}$ , is produced by heating equivalent weights of phenoxyacetic acid and aniline at  $150^{\circ}$ , and crystallising the product from hot alcohol; it forms long needles (m. p.  $99^{\circ}$ ), insoluble in cold water, but easily soluble in hot alcohol.

Fuming nitric acid reacts readily with phenoxyacetic acid, but without the production of a substituted nitro-compound; the main product of the action is dinitrophenol.

*Orthonitrophenoxyacetic acid*,  $\text{CH}_2(\text{O.C}_6\text{H}_4.\text{NO}_2).\text{COOH}$ , may be prepared by heating together sodium orthonitrophenolate with excess of sodium monochloroacetate, dissolving the fused mass in water, precipitating by addition of hydrochloric acid, and crystallising from hot water, after filtration through animal charcoal. The acid is with difficulty soluble in water, crystallising therefrom in regular octahedrons, which melt at  $156.5^{\circ}$ .

The salts of orthonitrophenoxyacetic acid resemble those of phenoxyacetic acid in crystalline form and solubility; the salts of the alkaline earth metals of the nitro acid are somewhat more soluble, and those of the heavy metals less soluble than the corresponding salts of phenoxyacetic acid. The sodium, barium, and copper salts of orthonitrophenoxyacetic acid are described.

*Paranitrophenoxyacetic acid* may be prepared by the same method as

that used for preparing the ortho-acid, only substituting sodium par-nitrophenolate for the ortho-compound. This acid crystallises in microscopic forms, belonging either to the rhombic or to the monoclinic system (m. p. 183°). The properties of the acid and its salts resemble those of the ortho-acid.

By the action of reducing agents, paranitrophenoxyacetic acid appears to yield an amido-acid, easily decomposable by water; whilst the ortho-acid yields an anhydride,  $C_6H_7NO_2$  (m. p. 143—144°), analogous to oxindole, which is obtained by the action of reducing agents on the orthonitro-derivative of phenylacetic acid.

The action of bromine-water on a hot aqueous solution of phenoxy-acetic acid appears to give rise to more than one isomeric compound. By dropping bromine into a solution of ethyl phenoxyacetate in carbon bisulphide, boiling the product with soda, decomposing with hydrochloric acid, and crystallising from hot water,

*Monobromophenoxyacetic acid*,  $CH_2(O.C_6H_4Br).COOH$ , is obtained in brilliant rhombic plates (m. p. 153—154°). This acid is scarcely soluble in water, but is easily dissolved by alcohol. That the bromine is substituted in the phenyl group is shown by the fact that boiling with caustic alkali does not cause the bromine to be displaced by hydroxyl. A few of the metallic salts and the ethyl salt of the acid are described.

No phenoxybromacetic acid could be obtained by the direct action of bromine on phenoxyacetic acid, even in sealed tubes at 150°.

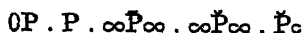
M. M. P. M.

**Action of Fused Alkalis on Aromatic Sulphonic Acids.** By P. DEGENER (*J. pr. Chem.* [2], 20, 300—320).—From the results of the action of fused potash and soda on phenolorthosulphonic and benzenedisulphonic acids respectively, the author concludes that the exchange of  $SO_3H$  for  $OH$  is brought about at a lower temperature, with a smaller quantity of alkali, and in shorter time by the use of potash than of soda; but if continued for a considerable time, the difference between the actions of the alkalis becomes less. In many reactions, the use of soda is preferable to that of potash, as the secondary reactions which frequently occur when the latter is used do not take place. The difference between the action of soda and potash is less marked in the replacement of  $SO_3H$  by  $OH$ , than in reactions which involve a more complete molecular decomposition, e.g., the production of salicylic acid from phenol.

M. M. P. M.

**Sulphanilic Acid.** By C. LAAR (*J. pr. Chem.* [2], 20, 242—267).—Besides the ordinary rhombic crystals with 1 mol. of water, the author describes a monoclinic form of sulphanilic acid, which crystallises from very dilute solutions with 2 mols. of water.

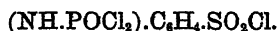
The crystalline forms of many metallic salts of the acid are detailed. The sodium salt,  $C_6H_4(NH_2)SO_3Na + 2H_2O$ , crystallises from concentrated solutions in leaf-shaped crystals, and from dilute solutions in plates, both belonging to the rhombic system,



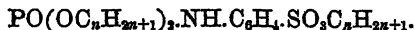
The *potassium* salt, with  $1\frac{1}{2}\text{H}_2\text{O}$ , forms rhombic prisms; the *ammonium* salt also crystallises in rhombic prisms, with  $1\frac{1}{2}$  mols. of water. The *barium* salt,  $[\text{C}_6\text{H}_4(\text{NH}_2).\text{SO}_3]_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ ; rhombic prisms,



the *copper* salt,  $[\text{C}_6\text{H}_4(\text{NH}_2).\text{SO}_3]_2\text{Cu} + 4\text{H}_2\text{O}$ , does not give off water at  $100^\circ$ . The *aniline* salt,  $[\text{C}_6\text{H}_4(\text{NH}_2).\text{SO}_3\text{H}].\text{C}_6\text{H}_7\text{N}$ , crystallises in needles, and is dissociated on boiling with water. When the dry salt is heated to  $150^\circ$ , the aniline is removed, and the free acid remains. By the action of phosphorus pentachloride on sulphanilic acid, under dry benzene, small colourless crystals are obtained, soluble in ether and hot chloroform, and having the composition



This chloride is decomposed by ethyl or methyl alcohol, with formation of the ethyl or methyl salt of *phosphanilidesulphonic acid*,



Both salts are soluble in the ordinary solvents, with the exception of carbon bisulphide and petroleum ether. The *phosphanilidesulphonic chloride*, mentioned above, is better prepared by heating phosphorus pentachloride with potassium sulphanilate on the water-bath, dissolving in absolute alcohol, and precipitating with water. After purification, the chloride forms small leaf-shaped crystals (m. p.  $102^\circ$ ).

Ethyl phosphanilidesulphonate is decomposed by boiling water, with production of sulphanilic acid, alcohol, and ethyl phosphate.

An oily diazo-compound, which has not yet been further examined, is produced by the action of nitrous acid on the same compound.

The action of phosphorus pentachloride on dibromosulphanilic acid gives rise to a chloride which is decomposed by ethyl alcohol, in a manner not exactly analogous to that noticed in the case of the chloride of sulphanilic acid, inasmuch as the compound formed still contains the group  $\text{SO}_2\text{Cl}$ , and has the formula



But along with this chloride, small quantities of the *ethyl salt* of *dibromophosphanilidesulphonic acid*,  $\text{PO}(\text{OEt})_2.\text{NH}.\text{C}_6\text{H}_2\text{Br}_2.\text{SO}_2\text{Et}$  are produced.

When potassium dimethylsulphanilate is heated with phosphorus pentachloride and alcohol is added, the product consists simply of the ethyl salt of the original acid, *i.e.*, of ethyl dimethylsulphanilate,  $\text{NMe}_2.\text{C}_6\text{H}_4.\text{SO}_2\text{Et}$ . This compound is easily soluble in benzene, chloroform, and acetone, and moderately soluble in ether and carbon bisulphide; it crystallises in small brilliant scales, which melt at  $85^\circ$ .

*Barium dimethylsulphanilate*,  $(\text{NMe}_2.\text{C}_6\text{H}_4.\text{SO}_3)_2\text{Ba}$ , crystallises in needles with 3 mols. of water,  $0\text{P} \cdot \text{P}\infty \cdot \infty\text{P}$ , or in plates with 11 mols.,  $0\text{P} \cdot \text{P}$ ; the latter form readily loses 8 mols. of water, and changes into the former.

\* The author believes this to be the first instance of an atomic compound containing eight different elements.

Potassium sulphanilate is readily oxidised in the cold by an aqueous solution of potassium permanganate to *potassium azophenyldisulphonate*,  $\text{SO}_3\text{K} \cdot \text{C}_6\text{H}_4\text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{SO}_3\text{K} + 2\frac{1}{2}\text{H}_2\text{O}$ , a salt which is but slightly soluble in cold water, and seems to belong to the class of colouring matter known as tropaeölms.

M. M. P. M.

**Trimethylparamidobenzenesulphonic Acid.** By P. GRIESS (*Ber.*, 12, 2116—2117).—The author proposes the name of "betaines" for a peculiar class of bases derived from the amido-acids of the benzoic acid and fatty acid series by replacement of three atoms of hydrogen by methyl. Amido-acids which contain the  $\text{SO}_3\text{H}$  group in place of carboxyl, also yield similar bodies, one of which may be obtained as follows:—Paramidobenzene-sulphonic acid is dissolved in a strong solution of potash, and after dilution with methyl alcohol, excess of methyl iodide is added. The alcohol is next removed by distillation, and the residue is mixed with a solution of iodine in hydriodic acid, by which means the base is obtained as a periodide in the form of gold-green tabular crystals. The periodide is decomposed by sulphuretted hydrogen, the solution neutralised with ammonia, and evaporated until it crystallises. The crystals thus obtained consist of brilliant, white, four-sided plates, which dissolve readily in water, but are almost insoluble in alcohol, and completely insoluble in ether. They have an extremely bitter taste and a neutral reaction. Trimethylparamidobenzenesulphonic acid has probably the constitution expressed by the formula  $\text{C}_6\text{H}_4\text{N}(\text{NMe}_2)_3\text{SO}_2\text{O}$ . It is a much weaker base than trimethylamidobenzoic acid, inasmuch as it does not form simple salts with acids; but it forms a well characterised aurochloride, and platinochloride,  $(\text{C}_6\text{H}_4\text{NMe}_3\text{SO}_2\text{HCl})_2\text{PtCl}_4 + 8\text{H}_2\text{O}$ . The latter crystallises in thin, yellowish-red, hexagonal plates, which are readily soluble. The new acid above described is decomposed when heated, and yields a heavy, oily base, together with much carbonaceous residue.

G. T. A.

**Phenyl-lactimide.** By E. POSEN (*Annalen*, 200, 97—99).—Amido-hydrocinnamic acid (*Annalen*, 195, 143; this Journal, Abst., 1879, 378) crystallises unchanged from dilute hydrochloric acid, but a hydrochloride,  $\text{PhCH}_2\text{CH}(\text{NH}_2)\text{COOH} \cdot \text{HCl}$ , can be obtained by dissolving the amido acid in warm hydrochloric acid diluted with its own bulk of water, and pouring the solution into three times its volume of fuming hydrochloric acid. The new compound is deposited in glistening prisms which dissolve freely in water.

When amidohydrocinnamic acid is treated with a mixture of equal volumes of water and sulphuric acid at  $60-70^\circ$ , it is converted into

*phenyl-lactimide*,  $\text{PhCH}_2\text{CH}(\text{NH})\text{CO}$ , or  $\text{CPhH}(\text{NH})\text{CH}_2\text{CO}$ . This substance

crystallises in silky needles (m. p.  $146^\circ$ ), soluble in alcohol, ether, carbon bisulphide, and hot water. Attempts to prepare metallic amidohydrocinnamates were unsuccessful.

W. C. W.

**Constitution of Anthraquinone.** By H. v. PECKMANN (*Ber.*, 12, 2124—2128).—Following a method similar to that adopted by Graebe in determining the constitution of naphthalene (*Annalen*, 149, 20), the author shows that in anthraquinone the pair of carbon-atoms is combined with both of the benzene-groups in the ortho-position. Since the oxyanthraquinones which contain hydroxyl in one benzene-nucleus yield on oxidation phthalic acid, it follows that in this reaction the nucleus containing hydroxyl in place of hydrogen is destroyed, and that the other must contain the carbon pair in the ortho-position. For the ortho-position of the carbon pair in the other benzene group, a proof was found by preparing an oxyanthraquinone which had undergone substitution in the benzene nucleus containing the two carbon-atoms in the ortho-position, and obtaining from it by oxidation phthalic acid, whilst still retaining the other benzene group. Orthobromophthalic acid was first prepared and then converted by the action of benzene and aluminium chloride into orthobromobenzoylbenzoic acid. This acid contains bromine in place of hydrogen in the benzene-group with which both the CO-groups are combined in the ortho-position. The orthobromobenzoylbenzoic acid, when acted on by concentrated sulphuric acid, yielded an orthobromanthraquinone, from which phthalic acid was obtained by the action of nitric acid.

This orthobromanthraquinone by the action of potash is converted into an oxyanthraquinone, having the same properties, except the melting point ( $190^{\circ}$ ), as the erythroxyanthraquinone of Baeyer and Caro (*Ber.*, 7, 968). The two bodies were also found to give almost identical results when examined by the spectroscope.

Since Liebermann obtained erythroxyanthraquinone (m. p.  $190^{\circ}$ ) by reduction of quinizarin, the hydroxyl must occupy the ortho-position with respect to the ketone-group, and therefore the bromine-atom must occupy the same position in the bromanthraquinone above described.

G. T. A.

**Action of Haloid Acids on Isoprene. Formation of Caoutchouc.** By G. BOUCHARDAT (*Compt. rend.*, 89, 1117—1120).—Isoprene, obtained by the dry distillation of caoutchouc, combines with hydrochloric acid gas to form the chloride  $C_5H_7Cl$  (b. p.  $86-91^{\circ}$ , sp. gr. 0.868 at  $16^{\circ}$ ), which is converted by the action of moist silver oxide into an alcohol boiling between  $120^{\circ}$  and  $130^{\circ}$ . The chloride absorbs bromine vapour, forming the compound  $C_5H_7ClBr$ , which decomposes on distillation. When isoprene is treated with concentrated hydrochloric acid, a mixture of mono- and di-chlorides is formed, together with a solid compound, which appears to be identical with caoutchouc. The dichloride,  $C_5H_7Cl_2$ , boils between  $145^{\circ}$  and  $153^{\circ}$ , and has a sp. gr. of 1.065 at  $16^{\circ}$ . A saturated solution of hydrobromic acid has a similar action on isoprene; the monobromide,  $C_5H_7Br$ , boils at  $104-105^{\circ}$  (sp. gr. 1.175 at  $15^{\circ}$ ), and combines with 2 atoms of bromine. The dibromide,  $C_5H_7Br_2$ , boils at  $175-180^{\circ}$ , and is heavier than water (sp. gr. 1.601 at  $15^{\circ}$ ). When treated with potash, it loses half its bromine, and gives rise to a liquid which boils at  $110^{\circ}$ . The action of hydriodic acid on isoprene appears to be analogous to that of hydrochloric acid, but the products of the reaction were not obtained in a state of purity.

W. C. W.

**Relations of the Camphenes obtained from Borneol and from Camphor.** By J. KACHLER and F. V. SPITZER (*Annalen*, 200, 340—360).—The authors having independently prepared hydrocarbons,  $C_{10}H_{18}$ , the one from borneol chloride,  $C_{10}H_{17}Cl$ , the other from camphor dichloride,  $C_{10}H_{16}Cl_2$  (*Annalen*, 197, 86 and 126 resp.), have jointly investigated the question of their probable identity. The preparation of the former, by decomposing the chloride with warm water, has been several times repeated with uniformly the same result; the pure camphene melts at  $51-52^\circ$ , and boils at  $160-161^\circ$ ; these points are unaffected by recrystallisation. From the higher fractions, a small quantity of borneol was isolated; this is formed simultaneously with the camphene. The hydrochloride of the camphene was prepared by passing hydrochloric acid gas into its solution in anhydrous ether; it melts at  $156-157^\circ$ ; a column of 201.7 mm. of its solution in ethyl acetate (1 gram-molecule in 1,000 c.c.) caused a left-handed rotation of  $6.1^\circ$ . It is decomposed by warm water, with formation of the original camphene, and a small quantity of borneol. Its properties generally are those of borneol chloride. The hydrochloride of the second camphene was prepared in a similar manner; the product, however, was in the first instance impure, the chlorine being 1—3 per cent. below the theoretical, and this was not altered by prolonged contact with hydrochloric acid gas; by recrystallisation from alcohol and subsequent exposure in ethereal solution to the gas, a hydrochloride was obtained with the theoretical percentage of chlorine, melting at  $153^\circ$ , and yielding, on decomposition with water, a camphene melting at  $51.2^\circ$  and boiling at  $161^\circ$ . A column of 100.3 mm. of the molten camphene causes a right-handed rotation of only  $2.4^\circ$ , whereas that prepared directly from camphor dichloride gives, under similar circumstances, a rotation of  $50^\circ$ .

The results may be summed up as follows:—The camphene, of melting point  $51-52^\circ$ , obtained from borneol chloride by decomposition with water and fractionation of the product, is the pure hydrocarbon,  $C_{10}H_{18}$ , and yields directly, with hydrochloric acid, the pure hydrochloride,  $C_{10}H_{18}HCl$ ; that obtained by the action of sodium on camphor dichloride is in the first instance mixed with a hydrocarbon which does not combine with hydrochloric acid; the hydrochloride may be obtained pure by crystallisation, &c., and then yields on decomposition a camphene melting at  $51-52^\circ$ , which combines directly with hydrochloric acid to form a pure product identical with the first-named hydrochloride. It is therefore concluded that the camphenes in question are identical.

The next point investigated was the constitutional relationship of camphene hydrochloride to borneol. The hydrochloride was heated with silver acetate and glacial acetic acid in a sealed tube at  $70^\circ$ ; an acetate was obtained identical with that prepared by Banbigny (*Zeits. Chem.*, 1866, 408) and by Montgolfier (*Ann. Chim. Phys.* [5], 14, 5). On heating this with solid soda at  $120-150^\circ$ , a sublimate of pure borneol was obtained; the residue, on distillation with sulphuric acid, yielded acetic acid. It appears, therefore, that camphene hydrochloride is borneol chloride.

The formation of borneol in small quantity, which attends that of

camphene in the decomposition of borneol chloride by water, may be referred either to double decomposition between the constituents of the two latter causing the replacement of Cl by (OH), or to a hydration of camphene under the influence of the hydrochloric acid simultaneously formed. Qualitative experiments showed that camphene does, in effect, yield borneol on heating with dilute acids, and the authors, therefore, adopt the latter explanation.

The identity of the camphenes was borne out by the investigation of the products which they yield on oxidation with chromic acid. These were in both cases chiefly camphor, and in addition small quantities of camphoric and camphoronic acids, together with acetic and carbonic acids.

In conclusion, the authors observe with reference to the constitution of camphene, that it is an unsaturated hydrocarbon containing the atomic group peculiar to the camphor-group; yielding, by addition of oxygen, camphor, by addition of chlorine, camphor dichloride. (They anticipate soon being able to furnish direct proof of the latter point.) From the manner in which camphene is converted into camphor, it is probable that the oxygen of the latter is not present in the form of a CO-group, but rather that it is united by a single affinity to two carbon-atoms. The reactions of camphor are most completely to be expressed by a modified form of the formulæ proposed by V. Meyer and by Armstrong (*Ber.*, 3, 121, and 11, 1698 resp.), which the authors intend shortly to publish.

C. F. C.

**Palmellin and Characin Extracted from Algae by Water.** By T. L. PHIPSON (*Compt. rend.*, 89, 1078—1079).—Xanthophyll (the yellow colouring matter of leaves in autumn), chlorophyll, and palmellin, may be respectively extracted from *Palmella cruenta* by successive treatment with carbon bisulphide, alcohol, and water. The preparation of characin has already been described (this volume, 53).

W. C. W.

**Coto-barks and their Characteristic Ingredients.** By J. JOBST and O. HESSE (*Annalen*, 199, 17—96).—Two kinds of coto-bark are found in the market, both of which are exported from Bolivia: the one which was first examined comes from the interior of Bolivia, and from its resemblance to the true cinchona barks was called "Cinchona Coto." According to Wittstein, however, it would appear to be derived from some plant belonging to the orders Lauraceæ or Terebinthaceæ, rather than to the Rubiaceæ. The powder or tincture is used in cases of diarrhoea and colic, also for neuralgia, rheumatism, and gout. Another variety of coto-bark, said to come from the shores of the Mapiri, closely resembles the other in appearance, but its physiological action is considerably weaker. It is called by the authors "Paracoto-bark," and differs greatly from the true coto-bark in its chemical nature, for although piperonylic acid is found in both (this *Journal*, Abstr., 1878, 733) the cotoïn and dicotoïn contained in the true coto-bark are absent in paracoto-bark, being replaced by paracotoïn, hydrocotone, dibenzoylhydrocotone, leucotin, and oxyleucotin. As the two barks very closely resemble one another in appearance, and are sold under the common appellation of "coto-bark," the crystallised



cotoïn of commerce manufactured from them necessarily varies greatly in its physiological effects, according as it is prepared from the true or false coto-bark or mixtures of the two.

*Cotoïn*.—The method of preparing this compound, which is only contained in true coto-bark, has already been described (this Journal, 1877, i, 480). Its melting point is  $130^{\circ}$ , and its solutions have no action on polarised light. The results of the analyses of the substance itself, and of the lead compound, correspond very closely with the formula  $C_{22}H_{18}O_8$ . The action of bromine in chloroform solution gives rise to *tribromocotoïn*,  $C_{22}H_{15}Br_3O_8$ ; this crystallises in yellow prisms (m. p.  $114^{\circ}$ ), almost insoluble in cold water, but easily soluble in alcohol. *Triacetylcotoïn*,  $C_{22}H_{15}Ac_3O_8$ , is formed by the action of acetic anhydride on cotoïn at  $170^{\circ}$ : it forms large prisms (m. p.  $94^{\circ}$ ) easily soluble in chloroform, in ether, and in hot alcohol. Benzoic acid is formed when cotoïn is heated with concentrated hydrochloric acid at  $140^{\circ}$ , also when it is fused with potash.

*Dicotoïn*,  $C_{44}H_{34}O_{11}$ .—When the crude cotoïn is treated with boiling water, at first nothing but cotoïn crystallises out from the cooled solution, but when the insoluble residue is treated again and again with the mother-liquors, large plates make their appearance: these may be to a great extent separated from the cotoïn by means of a sieve which retains the plates. When pure, it melts under boiling water, and is but sparingly soluble in it; by boiling with water, however, it appears to be converted into cotoïn. Dicotoïn crystallises in lustrous, almost colourless plates (m. p.  $74-77^{\circ}$ ), easily soluble in alcohol, ether, and chloroform.

*Paracotoïn*,  $C_{19}H_{12}O_8$ .—This compound, which melts at  $152^{\circ}$ , has already been described (this Journal, 1877, ii, 201). When bromine is gradually added to a chloroform solution of paracotoïn, it is at first absorbed, with evolution of hydrobromic acid, but on continuing the addition of bromine, a scarlet crystalline precipitate is formed, which, on being dried between filter paper becomes yellow, whilst hydrobromic acid continues to be given off. The analyses agree with the formula,  $C_{19}H_{11}Br_3O_{12}$ , but it is probably a brominated derivative of paracotoïn, as when gently heated with potash-solution, it yields the characteristic odour of paracoumarhydrin, a substance produced on decomposing paracotoïn itself with potash (*loc. cit.*). *Paracotoïc acid*, as already noticed, is produced by the action of baryta-water on paracotoïn, but may be more conveniently prepared by means of potash. The solution is first treated with ether to remove paracoumarhydrin, and the crude paracotoïc acid may then be precipitated with hydrochloric acid. When pure, it melts at  $108^{\circ}$ ; its barium, calcium, lead, and silver salts are yellow amorphous precipitates.

*Leucotoïn*,  $C_{34}H_{22}O_{10}$  (*loc. cit.*).—When leucotoïn is treated with bromine in chloroform solution at the ordinary temperature, it yields *dibromoleucotoïn*,  $C_{34}H_{20}Br_2O_{10}$ , crystallising in small white prisms (m. p.  $187^{\circ}$ ), very sparingly soluble even in boiling alcohol, more soluble in ether or chloroform. When gently heated with excess of bromine in acetic acid solution for a long time, it is converted into *tetrabromoleucotoïn*,  $C_{34}H_{18}Br_4O_{10}$  (m. p.  $157^{\circ}$ ).

*Cotagenin*,  $C_{14}H_{14}O_6$ .—When leucotoïn is fused with potash, it gives

off hydrogen, and the product contains benzoic acid, and small quantities of formic and protocatechuic acids, protocatechuic aldehyde and cotogenin. In order to extract the latter, the solution of the fused mass is acidified with hydrochloric acid and treated with ether: the ethereal solution is then agitated with soda to remove the acids, and evaporated. The protocatechuic aldehyde and the cotogenin in the crystalline residue are separated by means of alcohol, in which the last-named substance is but sparingly soluble. After being purified by crystallisation from boiling acetic acid, cotogenin melts at  $210^{\circ}$ , but at the same time turns brown and decomposes; at a higher temperature, pyrocatechol distils over. When fused with potash, it is entirely decomposed into protocatechuic acid, whilst hydrogen is given off in abundance. Attempts to prepare a bromine-derivative of cotogenin were unsuccessful.

*Hydrocotone*,  $C_{18}H_{24}O_6$ .—When the fusion of the leucotin with potash takes place in a retort, an oil distils over which solidifies on standing. The hydrocotone thus obtained may be easily purified by distillation or by crystallisation from alcohol, in which it is readily soluble, as well as in ether and in chloroform: it is but sparingly soluble in boiling water, and almost insoluble in potash solution. It forms colourless prisms (m. p.  $48-49^{\circ}$ ; b. p.  $243^{\circ}$ ). When gently heated with nitric acid, it is converted into *dinitrocotone*,  $C_{18}H_{20}(NO_2)_2O_6$ . This compound crystallises in plates which explode when strongly heated. It dissolves in water, alcohol, and concentrated nitric or hydrochloric acid with magnificent blue colour. The author considers hydrocotone to be a substance of the nature of a quinol, whilst dinitrocotone is probably a dinitro-derivative of the corresponding quinone. The formation of hydrocotone and cotogenin from leucotin may be represented by the equation  $C_{34}H_{38}O_{10} + 5H_2O = C_{18}H_{24}O_6 + C_{14}H_{14}O_5 + 2CH_2O_2$ , whilst the benzoic acid is produced thus:  $C_{34}H_{38}O_{10} + 4H_2O = C_{18}H_{24}O_6 + 2C_7H_6O_2 + 2CH_2O_2$ .

*Oxyleucotin*,  $C_{34}H_{38}O_{12}$  (*loc. cit.*).—Protocatechuic acid is found amongst the products of the action of concentrated hydrochloric acid on oxyleucotin at  $140^{\circ}$ . *Dibromoxyleucotin*,  $C_{34}H_{30}Br_2O_{12}$ , and *tetrabromoxyleucotin*,  $C_{34}H_{22}Br_4O_{12}$ , are colourless crystalline substances melting at  $190^{\circ}$  and  $159^{\circ}$  respectively: they may be obtained by a process similar to that described for the corresponding leucotin derivatives. When oxyleucotin is fused with potash, it yields the same products as leucotin.

*Dibenzoylhydrocotone*,  $C_{32}H_{32}O_8$ , is contained in the crude leucotin, and is left undissolved on treating it with a small quantity of acetic acid. When purified by crystallisation from hot acetic acid, it forms colourless prisms (m. p.  $113^{\circ}$ ) easily soluble in chloroform, ether, or boiling alcohol. When fused with potash, it is in great part resolved into hydrocotone and benzoic acid, but some cotogenin is produced at the same time. *Dibromodibenzoylhydrocotone*,  $C_{32}H_{24}Br_2O_8$ , formed on adding bromine to an acetic acid solution of dibenzoylhydrocotone, crystallises in colourless prisms (m. p.  $147^{\circ}$ ), and is converted into *tetrabromodibenzoylhydrocotone*,  $C_{32}H_{16}Br_4O_8$  (m. p.  $84^{\circ}$ ), by treating it with excess of bromine in chloroform solution.

*Hydrocotom*,  $C_{18}H_{14}O_4$  (*loc. cit.*), yields two bromine derivatives, of

which *monobromhydrocotoin*,  $C_{15}H_{13}BrO_4$ , crystallises in pale yellow needles and very short monoclinic prisms (m. p.  $147^\circ$ ), whilst *dibromhydrocotoin*,  $C_{15}H_{13}Br_2O_4$ , forms sulphur-yellow six-sided prisms (m. p.  $95^\circ$ ). *Acetylhydrocotoin*,  $C_{15}H_{13}AcO_4$ , obtained by the action of acetic anhydride on hydrocotoin at  $150^\circ$ , forms colourless crystals (m. p.  $83^\circ$ ), which yield a crystalline monobrominated derivative (m. p.  $166^\circ$ ). When heated with potash, hydrocotoin yields hydrocotone and benzoic acid.

An account of the piperonylic acid existing in paracoto-bark and of the various derivatives obtained from it, has already appeared (this Journal, Abstr., 1878, 733).

The *etheral oil* obtained by distilling paracoto-bark with water appears to differ somewhat from that existing in true coto-bark. By fractional distillation, it was separated into five portions, two of which, named  $\alpha$ - and  $\beta$ -paracotene, are hydrocarbons boiling at  $160^\circ$  and  $170^\circ$  respectively: the analyses and the fact that they do not absorb hydrochloric acid, show that they are not terpenes. The other three portions,  $\alpha$ -,  $\beta$ - and  $\gamma$ -paracotol are oxygenated oils boiling at  $220^\circ$ ,  $236^\circ$ , and  $240^\circ$  respectively. Full details of the physical properties and action of reagents on these five compounds are given in the paper.

In conclusion, the authors state that the various constituents of the coto-barks may be arranged in three groups.

The first, or hydrocotone group, includes hydrocotone, which is a hexhydric alcohol, dibenzoylhydrocotone, leucotin and oxyleucotin; the three last-named yield cotogenin and hydrocotone when fused with potash.

The second, or cotoin group, includes cotoin, dicotoin, and hydrocotoin, which are distinguished by giving a dark brown-red coloration with ferric chloride in alcoholic solution.

The third, or paracotoin group, contains but two members, paracotoin and paracotoic acid. Both these compounds give a deep yellow or brown-yellow coloration with concentrated nitric acid.

Besides these compounds, piperonylic acid, which had been already prepared by synthesis, exists ready formed in the bark, and also various oily bodies volatile in the vapour of water. C. E. G.

**Cinchona-barks.** By O. HESSE (*Annalen*, 200, 302—310).—This is a continuation of previous researches (*Annalen*, 185, 296) into the characteristics and identity of the bark of a variety of cinchona, the cusco-bark. A comparative analysis of a specimen of the *Quinquina jaune de Cusco* of Delondre and Bouchardt (obtained from *C. pelletierana*), which the author found to contain 0.37 per cent. cusconine, 0.24 aricine, no traces of quinine, and 0.50 of an amorphous alkaloid (in all 1.11 per cent. alkaloids), showed the close mutual resemblance of these varieties. The amorphous alkaloid present in the latter appears to be identical with the cusconidine previously isolated by the author from the cusco-bark (*Ber.*, 10, 2162). It is soluble in acetic acid, and is precipitated from the concentrated solution on the addition of nitric acid, as nitrate, in the form of brownish drops.

From a cusco-bark, presented some time since by J. E. Howard

to the Pharmaceutical Society, and obtained according to Holmes, from *C. pelletierana*, the author has isolated two new alkaloids, which he terms cuscamine and cuscamidine. A determination of the quantities of alkaloids present gave the following numbers: 0.21 per cent. aricine, 0.35 per cent. cusconidine, and 0.78 per cent. of a mixture of the new alkaloids. These were separated as nitrates, by adding nitric acid in small quantity to their solution in dilute acetic acid. They are separated from one another by taking advantage of the difference of solubility of the oxalates, cuscamine oxalate being comparatively insoluble in water. Cuscamine is readily isolated from the oxalate, and after recrystallising from alcohol is obtained in colourless prisms (m. p. 218°). These are dissolved by sulphuric acid to a yellowish solution, which changes to brown on warming; if molybdic acid be also present, a bluish-green colour is developed, changing to brown on warming, this again becoming violet-brown on cooling. The crystals are dissolved by concentrated nitric acid to a yellow solution, which does not alter on standing. The characteristics of several of the compounds of this alkaloid are described.

*Hydrochloride*, gelatinous and transparent, easily soluble in water.

*Aurochloride*, a yellow amorphous precipitate.

*Platinochloride*, yellow and flocculent, difficultly soluble in water.

*Hydrobromide* crystallises in large colourless plates.

*Hydriodide* crystallises from hot aqueous solution in microscopic needles.

*Nitrate* crystallises in needles which are almost insoluble in water.

*Sulphate* crystallises in needles, the hydrogen sulphate in prisms.

*Oxalate* crystallises in white needles, which are freely soluble in hot water, only slightly in cold.

The second alkaloid, cuscamidine, closely resembles cuscamine in its properties, the only important difference between them being that the former is precipitated by nitric acid from dilute, cuscamidine only from its concentrated solution.

The species of cinchona, *C. pelletierana*, from which the above alkaloids are obtained, has the additional characteristic of yielding neither quinine, cinchonine, quinamine, nor paricine, and is therefore to be regarded as extraordinary. The author suggests that in the classification of the cinchona group, regard should be paid to chemical as well as morphological characteristics.

C. F. C.

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## Physiological Chemistry.

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**Nutritive Value of Grass at Various Stages of Growth.** By E. v. WOLFF and Others (*Bied. Centr.*, 1879, 736—744).—The grass was cut three times in the early summer, in the years 1874 and 1877; the first cutting took place about the middle of May, the second at the beginning and the third at the end of June. The second cutting appeared to give the best results in the case of the animals experi-

mented upon, namely, sheep and horses; and as a rule it was found that more nitrogenous matter was excreted by the latter than by the former.

J. K. C.

**Nutritive Value of Asparagine.** By H. WEISKE and Others (*Bied. Centr.*, 1879, 744—748).—Asparagine when given in conjunction with glue, was found to support life in the case of rabbits and sheep, the latter digesting about twelve per cent. of the nitrogen.

J. K. C.

**Digestive Power of Geese for Fibrin.** By H. WEISKE (*Landw. Versuchs.-Stat.*, 24, 211—213).—Geese, according to the author's former researches, are not able to digest the fibrin of dandelion or horsetail. In order to confirm this result, analyses were made of the fibrin of the food and of the faeces, showing the composition to have remained unaltered.

J. K. C.

**Ptyalin and Diastase.** By T. DEFRESNE (*Compt. rend.*, 89, 1070).—Ptyalin converts starch into sugar in presence of impure gastric juice, as rapidly as it does in the mouth. Its action is, however, suspended by pure gastric juice, but on passing into the duodenum the ptyalin again becomes active. Diastase on the other hand is completely deprived of its power of converting starch into sugar, by hydrochloric acid, or by pure gastric juice.

W. C. W.

**Carbonic Anhydride from Muscle.** By R. STINZING (*Pflüger's Archiv. f. Phys.*, 20, 189—200).—Muscle of rabbits was employed. Every precaution was taken in the experiments, which were conducted by passing either air or nitrogen through boiling water containing the muscle. When air was employed 18.3 per cent., by volume, of carbonic anhydride was obtained as the mean of several experiments, and 15.8 per cent. when nitrogen was used. Mean of all experiments = 17.2.

M. M. P. M.

**Milk-secretion and the Amount of Fat in Milk.** By W. FLEISCHMANN and P. VIETH (*Landw.-Versuchs. Stat.*, 24, 81—97).—The absence of an extended series of such observations upon a large number of cattle induced the authors to avail themselves of an opportunity of making and recording certain investigations upon the herd of Count von Schlieffen, consisting of 119 cows. They observed and registered the daily yield of milk, the percentage of fat, the specific gravity, and the difference between the morning and evening milkings, with which they combined the results of a change of fodder and general treatment. Their observations extended over a whole year, and should be of value to students in this branch of chemistry.

The herd was of the dun-red Mecklenburg breed; their average weight during the stall-feeding season being 453.5 kilos. Taking into account their dry period, a mean of 55 days per year for each cow, the milk production of the whole herd was 2582.34 kilos. each, or ignoring their dry time, the whole number, year in year out, averaged 2191.73 kilos. each animal, equal to 5.69 times its own living weight.

The winter stall-feeding lasted from the commencement of the

observations (1st January, 1878) until 15th May; pasturage upon the town commons, not very good land, commenced on 16th May and continued to 17th July, when the cattle were put upon stubble and after-grass; on 15th October they were again housed, and were stall-fed until the authors ceased their record. Their daily food from 1st January to 5th March consisted of 12 kilos. of chopped fodder, viz., one-fifth clover hay, one-fifth meadow hay, three-fifths oat and barley straw; together with 0.875 kilo. long oaten straw, 1 kilo. wheat bran, 1 kilo. cocoa cake. The same rations were continued to 15th May, with the single addition of 0.375 of fleshmeal; from 15th October to 31st December the rations consisted of 4.165 clover hay, 1.75 meadow hay, 5.985 oaten straw, all long,  $\frac{1}{2}$  kilo. cocoanut cake,  $\frac{1}{2}$  kilo. rye meal; the hay was of good quality, the straw had been hand threshed, and of course contained some grains of corn.

The herd had an epidemic of cow-pox from the middle of September until the beginning of November, every cow being more or less affected. During its prevalence, the milk fell off very considerably, those cows which were only slightly affected by the disease did not show any marked departure from the normal butter or cheese produce, but the skim milk and cheese made during this time suffered from not ripening. The milkings took place with great regularity at 5 o'clock morning and evening, and it was the custom of the dairy to exactly weigh the milk; the samples of 60 to 80 c.c. were carefully drawn from the dairy receptacles containing about 100 kilos. of well mixed milk, the general determinations were only made weekly, double experiments being generally made. Particular search was made for the brownish substance first extracted from milk by ether, by Mannetti and Musso (*Zeitschr. Anal. Chem.*, 16, 397).

The subjoined table shows the influence of the fodder and changes of location; the average of the evening shows a higher sp. gr. and fat than the morning milk, which, however, is larger in quantity, except during the third period, when the days were longest; the proportion of fats in the evening yield oscillated within wider limits than in the morning; from March to July the morning milk was richer in fats than in the evening, being the period of the greatest activity of the lacteal glands, which fell partly in the fleshmeal and partly in the grazing periods. Search was made for the brown substance in every determination; it was, however, found only five times in the morning and eight times in the evening; from other experiments the authors believe it to exist in considerable quantities in buttermilk to as large a proportion as 2.053 of the total weight.

The experiments were to be continued in 1879, and a report is promised.

| Periods.                       | Specific gravity. |          | Percentage of fat. |          | Remarks.                         |
|--------------------------------|-------------------|----------|--------------------|----------|----------------------------------|
|                                | Morning.          | Evening. | Morning.           | Evening. |                                  |
| Dec. 30, 1877, to Mar. 5, 1878 | 1·0811            | 1·0814   | 3·387              | 3·439    | Ordinary stall-feeding.          |
| Mar. 6 to May 15               | 1·0811            | 1·0816   | 3·373              | 3·365    | Addition of fleshmeal.           |
| May 16 to July 16              | 1·0819            | 1·0818   | 3·314              | 3·145    | Pasturage on commons.            |
| July 17 to Oct. 14             | 1·0819            | 1·0821   | 3·341              | 3·450    | Pasturage on clover after-grass. |
| Oct. 15 to Dec. 31             | 1·0818            | 1·0821   | 3·460              | 3·627    | Stall-feeding.                   |
| Day's average..                | 1·0817            |          | 3·395              |          |                                  |

| Periods.                       | Milk per cow. |              | Fat per cow. |              | Remarks.                         |
|--------------------------------|---------------|--------------|--------------|--------------|----------------------------------|
|                                | Morning.      | Evening.     | Morning.     | Evening.     |                                  |
| Dec. 30, 1877, to Mar. 5, 1878 | Kilos. 3·543  | Kilos. 3·304 | Kilos. 0·120 | Kilos. 0·115 | Ordinary stall-feeding.          |
| Mar. 6 to May 15               | 4·013         | 3·854        | 0·136        | 0·129        | Addition of fleshmeal.           |
| May 16 to July 16              | 4·285         | 4·393        | 0·143        | 0·138        | Pasturage on commons.            |
| July 17 to Oct. 14             | 3·357         | 3·268        | 0·112        | 0·112        | Pasturage on clover after-grass. |
| Oct. 15 to Dec. 31             | 2·648         | 2·469        | 0·092        | 0·090        | Stall-feeding.                   |
| Day's average..                | 7·091         |              | 0·286        |              |                                  |

J. F.

**Abnormal Composition of Human Milk.** By C. MARCHAND (*Bied. Centr.*, 1872, 769—770).—According to the author, the usual composition of human milk is as follows:—butter, 36·8; lactose, 71·1; protein, 17; salts, 2·04, and water 873 parts per thousand; when the amount of butter rises to above 52 parts, the milk is injurious to the child. The quantity of protein, which is much less than in cow's milk, cannot be exceeded without ill effects.

J. K. C.

**Occurrence of a Reducing Substance in the Urine of Herbivorous Animals.** By B. DEHMEL (*Landw. Versuchs.-Stat.*, 24, 44—48).—These experiments were undertaken in consequence of the isolation, by Hofmeister, and afterwards by Kaltenbach, of a reducing substance in the urine of recently confined women suffering from milk-fever, this substance after several recrystallisations giving the reactions of milk-sugar. It was therefore thought desirable to ascertain if a stoppage of milk caused the same effect in animals. A goat which produced daily 5 litres was left unmilked for some days until a decided suppression of milk was obtained; the urine collected at intervals of 14—24 hours, each day's collection being sub-

mitted to examination with the result of finding an amount of the substance, which calculated as milk-sugar gave in proportion per 1,000 parts:—first day's sample, 0.492; the second day's, 0.401; the third, 0.231. The substance, after drying over sulphuric acid, appeared as a glassy yellowish mass without any trace of crystalline structure. Subjected to dialysis the reducing body passed freely into the dialysate, and on again evaporating this liquid, the same vitreous amorphous substance was reproduced. In order to compare the results with the kidney secretions of a non-milk-producing animal, the urine of an ordinary wether sheep was collected and treated in the same way, with the result of obtaining on the first day a proportion per 1,000 of 0.137; at the end of the second 0.124 of the substance reckoned as milk-sugar.

The quantity found in the urine of the goat in this case was trifling, and does not come near the amount obtained by Hofmeister from the woman's urine; the amount found in the milk-producing animal at the beginning of the experiment was, however, about four times that found in the male animal, but at the end of the third day it was not double.

The author is not certain that the substance is milk-sugar; he only considers it proved that it is a strongly reducing dextrorotatory substance.

J. F.

**Analysis of Concretions taken from an Abscess on the Jawbone of a Horse.** By G. THOMS (*Landw. Versuchs.-Stat.*, 24, 49).—The concretions were of irregular form, of a whitish colour, with a red-brown shade of blood corpuscles; in one instance they had formed round a particle of straw, so that the author concludes that the abscess and concretions were caused by a wound sustained by the animal in taking its food. The principal constituent was calcium carbonate.

J. F.

**Action of Dehydrating Agents on the Crystalline Lens of the Eye.** By E. HEUBEL (*Pflüger's Arch. f. Phys.*, 20, 114—188).—The general result arrived at by the author is that cataract may be artificially produced in frogs, and also in warm-blooded animals, by the introduction into the eye of substances which act as dehydrating agents, and that the action of these bodies is physical, depending as it does on a process of osmose between the saline liquid in the aqueous humour and vitreous body, and the water in the lens, whereby the amount of the latter is reduced, whilst simultaneously a small quantity of the salt injected finds its way into the lens. The action is confined to the eye itself, and is not, as supposed by Guttman, an action on the general organism. A list is given of a large number of potassium and sodium salts, &c., which cause cataract if injected into the eye of the frog or rabbit. Many sodium salts produce cataract when injected under the skin, while other salts do not act in this way under the same conditions. The author explains this by the facts that sodium salts are not readily expelled from the blood, because their rate of diffusion is comparatively low, and that their dehydrating action is not rapid; these salts therefore eventually find their way to the eye in a state in



which they are still capable of withdrawing water from the lens. Very many physiological details are given in the original, and the results of other workers are discussed at length. The author thinks that cataract in the human subject is caused by the presence in the aqueous humour and vitreous body of an excess of mineral matter which reacts on the lens and diminishes the amount of water therein.

M. M. P. M.

## Chemistry of Vegetable Physiology and Agriculture.

**The Butyric Ferment (*Bacillus Amylobacter*) in the Carboniferous Period.** By P. v. TIEGHEM (*Compt. rend.*, 89, 1102—1104).—*Bacillus amylobacter* is soon developed when fragments of the young roots of cypress or yew are immersed in water. It attacks the tissues and cellular membranes of the roots, dissolving the cellulose which undergoes butyric fermentation, and finally leaving nothing but the cuticle and the vessels. The different stages of development of the bacillus may be traced in the interior of the destroyed organ, from the slender threads in a state of active division to the free spores floating in the liquid which fills the space once occupied by the cells.

A microscopical examination of the numerous rootlets of coniferæ, found in the fossil state in the coal measures of St. Etienne, exhibits visible traces of the ravages committed by the *Bacillus amylobacter*.

W. C. W.

**Formation of Vinegar by Bacteria.** By E. WURM (*Dingl. polyt. J.*, 235, 225).—The author has investigated this matter, and his results prove, without doubt, that an active formation of vinegar from alcohol is obtained by means of *Mycoderma aceti* (*Bacterium mycoderma*—Cohn), thus supporting Pasteur's view. The author then discusses the practical details of the process given by Pasteur, and compares the process with others.

J. T.

**Starch-altering Ferments in Plants.** By J. BARANWITZKY (*Bied. Centr.*, 1879, 790—791).—Ferments were obtained from the germinating seeds of many plants and their action on starch examined. In many cases it was found possible to convert 70 per cent. of the starch into glucose. The author is of opinion that the starch is first converted into dextrin alone, and not into dextrin and glucose together.

J. K. C.

**Organisms in Beet Sap.** By L. CIENKOWSKI (*Beid. Cent.*, 1879, 767).—The bodies known as "frogspawn," which make their appearance after a time in the sap of beetroot, prove on microscopic examination to be a species of bacterium, called by the author *Ascococcus Biloithii*.

J. K. C.

**Carbonic Acid in the Air.** By MARIE-DAVY (*Compt. rend.*, 90, 32—35).—An examination of the determinations of the amount of

carbonic anhydride in the air, which have been made daily during the last four years at Montsouris, seems to show that the best crops have been produced in those years when the amount of carbonic anhydride has been below the average. The carbonic anhydride varies inversely with clearness of the sky, and is influenced by the oscillations of the great equatorial atmospheric currents. W. C. W.

**Respirative Power of Marsh and Water Plants.** By E. FREYBERG (*Bied. Centr.*, 1879, 748—750).—It is a well-known fact that these plants are able to thrive in media which contain little or no oxygen. They are all very poor in nitrogen, and the author has shown by a number of experiments that this latter property accounts for the former. His investigations prove that the respirative power of plants varies with the amount of nitrogen they consume, and this, taken in conjunction with the fact that water plants contain large air chambers which do not often need refilling, accounts for their being able to exist in media which contain very little oxygen.

J. K. C.

**Influence of Nutritive Material on the Transpiration of Plants.** By A. BURGERSTEIN (*Bied. Centr.*, 1879, 750—752).—The author shows that plants transpire more when placed in a 0·2 per cent. solution of any nutritive salt than in pure water alone, but that the transpiration diminishes as the percentage increases, also that if the 0·2 per cent. be made up of more than one salt the transpiration is less than in pure water.

J. K. C.

**Influence of Salicylic Acid and other Bodies on Germination.** By E. HECKEL (*Bied. Centr.*, 1879, 789).—Small doses of salicylic acid appear to have a favourable influence on the germination of seeds, whereas phenol and thymol have an opposite, although not a lasting effect.

J. K. C.

**Passage of Plant-material in Seedlings.** By W. DETMER (*Bied. Centr.*, 1879, 788—789).—Glucose by itself can pass only from cell to cell, and must enter into some combination before being able to pass through the septum of the plasma. Vegetable casein is insoluble in water, but is rendered soluble by organic acids and neutral alkaline phosphates.

J. K. C.

**Course of the Nitrogen and Mineral Constituents in the Development of the Early Shoots.** By J. SCHRÖDER (*Bied. Centr.*, 1879, 752—754).—It was found that from the 5th of April to the 18th of May the axial organs of the plants under investigation had lost a great quantity of their nitrogen and mineral contents, which had passed into the young shoots. In the cases of phosphoric acid, the loss was greatest, amounting to nearly 50 per cent.; nearly one-third of the potash, and more than one-fourth of the magnesia and nitrogen had also been given up. The amount of lime and silica was, however, greater at the end than the beginning of the period under observation, and as some at least had passed into the shoots, the roots must have been more active in absorbing these constituents.

J. K. C.

**Development of Oats.** By P. DEHÉRAIN and NANTIER (*Bied. Centr.*, 1879, 765—766).—Oats grown on land which had not been manured since 1875, showed a great falling off in the percentage of nitrogen, 3·12 per cent. of nitrogenous substances being found instead of 8 or 9 per cent. as usually obtained. With respect to the loss of weight which the plants undergo at the ripening period, the authors express their opinion that it is proportionate to the goodness of the crop. J. K. C.

**Influence of the Leaves on the Production of Sugar in the Beet.** By B. CORENWINDER and G. CONTAMINE (*Bied. Centr.*, 1879, 792).—The leaves of the beetroot contain small quantities of glucose, and those roots which have well-developed leaves are the richest in sugar. J. K. C.

**Ripening of Grapes.** By C. PORTELE (*Bied. Centr.*, 1879, 758—764; comp. this volume, p. 178).—The chief object of this series of investigations was to ascertain the changes which the acids of the grape undergo during the ripening process. Examinations were made of the must and aqueous extract of the Negrara grape at various times from the 26th of July to the 21st of October, 1878. The results show that the total quantity of free acid in the must and aqueous extract increases until the grapes begin to soften, and then regularly diminishes. The tannic acid disappears altogether in the must, but not entirely in the aqueous extract, as it is still present in the skins and seeds. The free tartaric acid, from the time the berries begin to soften, gradually diminishes, and finally disappears when the grapes are fully ripe. Malic acid is still present in the ripe berries, and then forms two-thirds of the total free acid: it is not found in the combined state. Sulphuric acid and phosphoric acid are present in the ash in sufficient quantity to combine with the lime and magnesia, whilst potash is found in excess of the amount required for the cream of tartar. The following table gives the weight in grams of the various constituents in 100 berries plucked at different times:—

|                    | Sugar. | Precipitate<br>with<br>alcohol. | Insoluble<br>in water. | Total<br>free acid<br>calculated<br>as tartaric. | Free<br>tartaric<br>acid. |
|--------------------|--------|---------------------------------|------------------------|--|---------------------------|
| 26th July.....     | 0·16   | 0·32                            | 1·19                   | 0·79   | 0·31                      |
| 6th „ .....        | 0·29   | —                               | 1·80                   | 1·14   | 0·41                      |
| 16th „ .....       | 0·41   | 0·65                            | 3·02                   | 2·09   | 0·78                      |
| 12th August .....  | 1·64   | 0·59                            | 5·28                   | 3·40   | 0·81                      |
| 23rd „ .....       | 16·00  | 1·08                            | 5·68                   | 2·51   | 0·65                      |
| 31st „ .....       | 21·70  | 1·15                            | 5·27                   | 2·12   | 0·30                      |
| 9th September..... | 28·60  | 1·16                            | 6·45                   | 1·83   | 0·25                      |
| 28th „ .....       | 31·20  | 1·28                            | 7·60                   | 1·54   | 0·04                      |
| 12th October ..    | 38·20  | 1·96                            | 7·96                   | 1·48   | 0·02                      |
| 21st „ .....       | 38·30  | 1·67                            | 7·45                   | 1·08   | —                         |

|                     | Cream of tartar. | Tartaric acid | Malic acid found. |            | Total free and combined tartaric acid. |
|---------------------|------------------|---------------|-------------------|------------|--|
|                     |                  |               | Directly.         | Indirectly |  |
| 26th July .....     | 0.19             | 0.23          | 0.35              | 0.31       | 0.46                                   |
| 6th " .....         | 0.27             | 0.48          | —                 | 0.15       | 0.61                                   |
| 16th " .....        | 0.13             | 0.39          | 0.90              | 0.92       | 1.12                                   |
| 12th August .....   | 0.47             | 0.68          | 2.17              | 2.00       | 1.19                                   |
| 23rd " .....        | 1.06             | 0.75          | —                 | 1.13       | 1.49                                   |
| 31st " .....        | 1.18             | 0.82          | 1.19              | 1.04       | 1.24                                   |
| 9th September ..... | 1.25             | 0.81          | 0.98              | 0.80       | 1.24                                   |
| 28th " .....        | 1.11             | 0.70          | 0.86              | 0.68       | 1.19                                   |
| 12th October .....  | 1.53             | 0.79          | 0.73              | 0.60       | 1.24                                   |
| 21st " .....        | 1.57             | 0.79          | 0.48              | 0.20       | 1.25                                   |

The grapes gathered on the 26th of July were from a very backward plant.

It appears from the above table, that the total quantity of tartaric acid remained pretty constant after the berries began to soften, the free acid being gradually neutralised by the potash, and thus disappearing.

Experiments on the after-ripening of grapes showed that the amount of sugar and tartaric acid in the berries remained constant, unless kept until decomposition set in: the malic acid, however, diminished in the same manner in the case of unripe grapes as if they were still attached to the vine stock.

J. K. C.

**Growth of Plants in Artificial Solutions.** By F. FARSKY (*Bied. Centr.*, 1879, 669—671).—The conclusions which the author draws from his experiments on the replacement of potash by soda in the plant, and the influence of various substances on the growth of plants, such as chlorine, chloride of calcium, &c., agree in all respects with former investigations.

J. K. C.

**Formation of Fat in the Growth of Fungi.** By C. v. NÄGELI and O. LÖRW (*J. pr. Chem.* [2], 20, 97—114).—Previous investigations of the phenomenon of the formation of fat in vegetable cells have established the following points:—That it is a secretion, and not a product of fermentation or other action external to the life of the cell; that it is formed in quantity varying with the activity of the growth, and of the oxygen respiration of the plant. On the chemistry of the process, especially in respect of the proximate sources of this product, but little light has been thrown. The fact that the starch which is present in the immature condition, *e.g.*, of the rape seed, is replaced in the mature condition by oil, has been regarded as the result of the conversion of the carbohydrates into fat; this conclusion is, however, unwarranted. There is weightier evidence of the origin of fat in the splitting up of cell proteids in the cells of penicillium and other fungi which are proteid in the earlier stages, and contain abundance of fat at later periods; the development of the latter is observed

to occur *pari passu* with a loss of proteïds; and since the cell-wall often undergoes considerable increase during the same periods, *i.e.*, carbohydrates are secreted, a causal connection between the former phenomena is extremely probable. The relation of fat formation to the nutrition of the plant is obscure, and throws no light on the problem; plants nourished with albuminoids evince a scarcely more active fat secretion than those fed on non-nitrogenous organic bodies (sugar, mannitol, glycerol, &c.), together with ammonia or nitric acid. The investigation of these and other points bearing on the question, is the purpose of the following experimental work:—

I. To determine the quantitative relations between the matter consumed as food, and that elaborated both in the aggregate, as cells with their contents and as fat.

Penicillium was selected as a simple cellular structure. The spores were sown in solutions (1—3 per cent.) of the several food-stuffs containing a sufficient quantity of ash constituents ( $K_2H_2PO_4$ ,  $MgSO_4$ , and  $CaCl_2$ ), and in addition 0·5—1 per cent. of free phosphoric acid, the presence of which is fatal to schizomycetes. The solutions were placed in flasks loosely closed with cotton wool, and agitated from time to time. After the expiration of several weeks the cells were filtered off, dried at 100°, and weighed; the filtrate evaporated and the residue weighed. The amount of organic matter consumed is the weight originally present less that of the residue. The fat was determined by weighing as fatty acid, after destroying the cell-walls with hydrochloric acid. The results are enumerated in the table (p. 339).

The conditions of growth, temperature, access of air, &c., were kept as constant and uniform as possible, so that those experiments in which the degree of concentration of the nutrient solution is the same may be regarded as strictly comparable.

In a second series the secretion of fat was more closely investigated in relation to nutrition by sugar and tartaric acid plus inorganic nitrogen on the one hand, and albumin, soluble and insoluble, on the other. The duration of the experiment was two months; at the end of this period the total growth of the penicillium and the fatty acids secreted by the cells were in each case determined. The details are tabulated below:—

| Nutrient solution.  | Total growth. | Fat acids per cent. of dry cells. |
|---|---------------|-----------------------------------|
| (a.) 500 c.c. water, 5 grams ammonium tartrate, 5 grams tartaric acid .....                                   | 0·540         | 8·08                              |
| (b.) 500 c.c. water, 50 grams sugar, 0·5 phosphoric acid, 5 grams potassium nitrate, 2 grams nitric acid..... |               |                                   |
| (c.) 300 c.c. water, 15 grams sugar, 3 grams ammonium tartrate, 3 grams tartaric acid.....                    | 2·301         | 12·35                             |
| (d.) 300 grams water, 3 grams peptone, 2 grams phosphoric acid.....   | 0·524         | 7·32                              |
| (e.) 300 c.c. water, 3 albumin, 2 phosphoric acid .....   | 0·531         | 8·79                              |
| (f.) 300 c.c. water, 3 albumin (insol.), 2 phosphoric acid ..   | 0·200         | 0·53                              |

| Nutrient solution.                 | Period of growth (days). | Consumption of food-stuff (grams). | Consumption per cent. of original weight. | Weight of organised product. | Assimilated per cent. of total consumption. | Consumed but not assimilated (burned). | Ratio assimilated to burned. | Fat acids per cent. of fungus. | Fat acids per cent. of total consumption. |
|------------------------------------|--------------------------|------------------------------------|---|------------------------------|---|--|------------------------------|--------------------------------|---|
| a. Ammonium tartrate 1 p. c. . .   | 56                       | 2.82                               | 56.4                                      | 0.308                        | 10.9  | 2.51                                   | 1:3.2                        | 6.67                           | 0.727                                     |
| b. Ammonium acetate 1.23 p. c. . . | 17                       | 1.96                               | 31.8                                      | 0.284                        | 14.5  | 1.68                                   | 1:5.8                        | —                              | —   |
| c. Ammonium succinate 1 p. c. . .  | 48                       | 2.7                                | 54.0                                      | 0.534                        | 19.8  | 1.17                                   | 1:4.5                        | 11.11                          | 2.199                                     |
| d. Ammonium tartrate 1 p. c. . .   | 60                       | 5.19                               | 51.9                                      | 0.518                        | 10.0  | 4.57                                   | 1:9.0                        | 7.58                           | 0.758                                     |
| e. Ammonium acetate 0.6 p. c. . .  | 84                       | 4.42                               | 49.1                                      | 0.940                        | 21.2  | 3.18                                   | 1:3.7                        | —                              | —   |
| f. Ammonium chloride 0.8 p. c. . . | 84                       | 7.4                                | 26.4                                      | 1.496                        | 20.2  | 5.91                                   | 1:4.0                        | 6.69                           | 1.351                                     |
| g. Asparagin 1 p. c. . . . .       | 56                       | 8.43                               | 69.6                                      | 0.795                        | 22.8  | 2.69                                   | 1:3.4                        | 7.06                           | 1.909                                     |
| h. Leucine 1 p. c. . . . .         | 28                       | 3.05                               | 61.0                                      | 0.905                        | 29.7  | 2.15                                   | 1:2.3                        | 11.5                           | 3.115                                     |
| i. Leucine 3 p. c. . . . .         | 28                       | 5.25                               | 35.0                                      | 1.130                        | 21.5  | 1.12                                   | 1:3.6                        | —                              | —   |
| k. Albumin 1 p. c. . . . .         | 52                       | 3.72                               | 74.4                                      | 0.861                        | 23.2  | 2.86                                   | 1:3.3                        | 11.25                          | 6.610                                     |
| l. Albumin 1 p. c. . . . .         | 52                       | 4.58                               | 45.8                                      | 1.124                        | 24.5  | 3.16                                   | 1:3.1                        | 12.22                          | 2.934                                     |
| m. Albumin 1 p. c. . . . .         | 48                       | 2.20                               | 22.0                                      | 0.563                        | 25.6  | 1.64                                   | 1:2.9                        | 14.92                          | 3.819                                     |
| n. Peptone 1 p. c. . . . .         | 55                       | 4.54                               | 44.5                                      | 1.101                        | 24.9  | 3.35                                   | 1:3.0                        | 14.83                          | 3.398                                     |
| o. Leucine 1 p. c. . . . .         | 51                       | 11.52                              | 76.8                                      | 2.873                        | 21.9  | 8.65                                   | 1:3.0                        | 17.66                          | 4.397                                     |
| p. Sugar 2 p. c. . . . .           | 52                       | 9.08                               | 60.5                                      | 2.984                        | 32.8  | 6.10                                   | 1:2.0                        | 18.10                          | 5.937                                     |

(The solutions contained in addition, 0.100 per cent.  $K_2H_2PO_4$ , 0.016  $MgSO_4$ , 0.005  $CaCl_2$ , 0.017  $(NH_4)_2SO_4$  in each case.)

In the case of (c) the residual sugar and tartaric acid were estimated in the filtrate; of the latter there remained 13.9 per cent. of the original weight, whereas of the sugar, although added in so much larger quantity, only 6 per cent. remained. No products of oxidation or fermentation could be detected.

II. To determine the formation of fat in relation to a varying supply of cane-sugar, that of nitrogen and the necessary inorganic salts being kept constant.

The solutions (1,000 c.c.) contained in each of the six experiments, 0.7 gram  $(NH_4)_2SO_4$ ; 2 grams  $K_2H_2PO_4$ ; 0.3 gram  $MgSO_4$ ; 0.1 gram  $CaCl_2$ ; and 0.9 gram phosphoric acid. The duration of growth was six weeks. The quantities of sugar and other details are given in the table:—

|                | Sugar<br>per cent. of<br>nutrient<br>solution. | Total<br>growth | Fat acids<br>per cent. of<br>cells. | Sugar<br>assimilated<br>per cent. of<br>total con-<br>sumption |
|----------------|--|-----------------|-------------------------------------|--|
| (a.) . . . . . | 0.1  | 0.210           | } 15.84 {                           | 34.3   |
| (b.) . . . . . | 0.5  | 0.305           |                                     | —  |
| (c.) . . . . . | 1.0  | 0.230           | —                                   | —  |
| (d.) . . . . . | 5.0  | 0.772           | 14.36                               | —  |
| (e.) . . . . . | 10.0   | 2.700           | —                                   | —  |
| (f.) . . . . . | 15.0   | 2.215           | 23.13                               | 8.8  |

The increase of yield, it will be seen, has no constant relation to the increase of concentration of the sugar solution. Comparison of (a) and (f) in respect to the quantity of sugar burned, shows that this increases with the concentration. As regards the inversion of sugar during the growth of penicillium, the authors found that in a 1 per cent. solution the growing plant caused the inversion of 60 per cent. of its weight (estimated as dry) of sugar in eighteen hours.

III. To investigate the "degradation" ("involution") of penicillium in relation to the fatty contents of the cells, one-fourth of the product of growth in a solution containing sugar (2 per cent.) and albumin (1 per cent.) was analysed in the fresh state (after drying); the remainder was placed in phosphoric acid solution (1 per cent.), and set aside for four weeks: the originally compact mass of hyphæ was by this time resolved into loose threads; these were filtered off, dried, and weighed, and found to represent about 15 per cent. of the original weight.

The following constituents were estimated:—

|                     | Before<br>degradation. | After<br>degradation. |
|---------------------|------------------------|-----------------------|
| Albumin. ....       | 42.7                   | 16.5                  |
| Fat. ....           | 18.5                   | 50.5                  |
| Cellulose, &c. .... | 38.8                   | 33.0                  |
|                     | <hr/> 100.0            | <hr/> 100.0           |

proving a considerable formation of fat at the expense of proteids.

The only general conclusion the authors at present draw from their results is, a classification of the nutrient matters investigated, in an ascending series representing the successive degrees in which they favourably influence the formation of fat, viz. (passing from those less to the more favourable), (1) ammonium acetate; (2) ammonium tartrate and succinate and asparagine; (3) leucine; (4) peptone; (5) ammonium tartrate, plus sugar; (6) leucine, plus sugar; (7) peptone, plus sugar.

The problem of the proximate origin of fats remains very much *in statu quo*. C. F. C.

**Formation of Vegetable Albumin.** By A. EMMERLING (*Landw. Versuchs.-Stat.*, 24, 113—160).—This long paper describes the author's investigations into the presence of albumin in the roots, stalks, leaves, blossoms, and seeds of the *Vicia faba maj.*, or common buff bean, with the view of throwing light upon the interesting and little known question of the production of proteid substances in plants, and how the nitrates and ammonium salts from the soil on the one side, and from decomposed nitrogenous organic substances on the other, are assimilated by the growing vegetable.

The author's experiments are very numerous, and show most careful and painstaking observation; his apparatus, of which he gives drawings, are eminently adapted to the purposes of his investigation, but they contain no new principle; and his results, although most interesting, being chiefly of a negative character, will be sufficiently understood from the summary with which he concludes the paper.

He finds the nitric acid taken up from the soil abundant in the roots and stems, gradually becoming less, until in the buds, blossoms, and fruits it is seldom to be met with, and he believes that the leaves are the particular organs charged with its transformation into albuminoids; that the most active agent is not nitrogen in the form of ammonium salts. As he has found the latter most frequently in the leaves from which the more active nitric compound had already disappeared, he thinks that had the ammonium salts been the most active agents, they would have been assimilated at an earlier stage. He thinks the absorbed nitrates, which are very unstable, are acted upon by the vegetable organic acids, which combine with the lime of the salt, and free the nitrogen, but he admits that his researches have not advanced our knowledge of the matter greatly, the only certain conclusion being that albumin is the result of the end reactions, of which we do not know the steps. The presence and distribution of the amides appear to point to a step in the process, as their distribution seems to follow a simple law, which is that those parts of the plant



which are of quickest growth, and which increase their bulk most rapidly, are invariably richest in amides. The young leaves contain more than old ones, the stem than the root. More particularly are the buds, sprouts, and blossoms rich in this product, and where new cells are about to be built up, there is previously collected upon the spot an accumulation of material for their construction, not only of the matters required to form their membranous portions, but of protoplasmic matter; it appears certain that the amides form the nourishment of the young cells; even the flower-buds accumulate these substances for the nourishment of the future seeds, but the manner in which the process is carried out still remains unknown. J. F.

**Leucine and Tyrosine in Potatoes.** By E. SCHULZE and J. BARBIERI (*Landw. Versuchs.-Stat.*, 24, 167—169).—The purified alcoholic extract from potatoes, when allowed to stand, was found to deposit after some time a crystalline substance, which on further examination proved to be impure tyrosine, giving all the characteristic reactions of that substance. The mother-liquor on further evaporation, and standing for a few days, yielded a crystalline crust of leucine.

J. K. C.

**Amount of Oil in Grass-seeds, and its Relation to their Germination.** By H. BREIHOLZ (*Bied. Centr.*, 1879, 756—757).—The various kinds of seeds examined contained oil in quantities varying from 0·8 to 15·8 per cent. Two hundred specimens of each sort were sown under the same conditions, and their germinating power and quickness of growth observed, the former of which, however, was found to bear no constant relation to the richness of the seeds in oil, whilst quickness of growth after a certain period was found to be to some extent dependent on the quantity of oil present.

J. K. C.

**Analysis of Parsnips.** By B. CORENWINDER and G. CONTAMINE (*Bied. Centr.*, 1879, 794). The following is the result of the analysis :—

|                             |       |
|-----------------------------|-------|
| Water.....                  | 79·34 |
| Nitrogenous substances .... | 2·36  |
| Crystallisable sugar .....  | 8·25  |
| Grape-sugar .....           | 1·57  |
| Fibre .....                 | 2·0   |
| Starch.....                 | 1·0   |
| Pectin, &c.....             | 4·33  |
| Mineral matter .....        | 1·02  |

---

 100·00

The ash contained 40 per cent. of potash, and 50 per cent. of phosphates.

J. K. C.

**Mineral Constituents of the Riesling Grape.** By A. HILGER (*Bied. Centr.*, 1879, 793).—The amount of dried substance was found to vary between 13 and 15 per cent., and the ash from 1·1 to 1·5 per cent. Analyses of the ash gave the following results :—

|                        | Riesling at<br>Stein. | Riesling at<br>Leisten. | Sylvaner at<br>Mulheim. |
|------------------------|-----------------------|-------------------------|-------------------------|
| Potash .....           | 33.04                 | 34.67                   | 48.46                   |
| Soda .....             | 1.84                  | 1.21                    | 0.45                    |
| Lime .....             | 8.55                  | 11.00                   | 7.33                    |
| Magnesia .....         | 2.61                  | 1.42                    | 3.75                    |
| Ferric oxide .....     | 1.04                  | 0.45                    | 0.10                    |
| Phosphoric acid .....  | 21.08                 | 19.72                   | 7.36                    |
| Sulphuric acid .....   | 4.54                  | 4.19                    | 4.89                    |
| Silica .....           | 1.00                  | 0.45                    | 1.71                    |
| Carbonic anhydride ..  | 22.51                 | 23.78                   | 24.38                   |
| Hydrochloric acid .... | 2.29                  | 2.53                    | 0.96                    |

J. K. C.

**Mineral Constituents of Fir and Birch.** By J. SCHBÖDER (*Bied. Centr.*, 1879, 754—756).—As regards the distribution of the ash of the fir in the tree, the author finds that the leaves are the richest, and that the bark is richer in ash than the wood. A concentration of the phosphoric, sulphuric, and silicic acid takes place in the direction of the branches, as these acids have a tendency to pass into the leaves. Magnesia and potash are found in largest quantities in the wood, and lime in the bark. Similar results were obtained in the case of the birch, as regards the distribution of the ash constituents, although not in so marked a degree. The fir gives more ash than the birch, the excess being due to the larger amount of silica present.

J. K. C.

**Ash Analyses.** By G. THOMS (*Landw. Versuchs.-Stat.*, 24, 53).—The ash of the seed capsules and stems of the flax plant were submitted to analysis, and compared with that of the hay of the *Galeopsis tetrahit*, or common "hollow tooth," a plant coming greatly into use as a fodder in Russia; the whole of the specimens were grown in Livonia. The following are the principal constituents:—

|                       | Potash. | Soda. | Lime. | Phosphoric<br>acid. | Silicic<br>acid. |
|-----------------------|---------|-------|-------|---------------------|------------------|
| Flax seed capsules .. | 22.39   | 6.69  | 27.41 | 25.14               | 5.21             |
| „ stems ....          | 19.75   | 0.56  | 31.84 | 8.85                | 15.87            |
| Galeopsis .....       | 41.26   | 1.75  | 23.43 | 9.74                | 10.79            |

J. F.

**Analyses of Feeding Stuffs.** By G. THOMS (*Landw. Versuchs.-Stat.*, 24, 50—52).—The author communicates the result of his examination of nine samples of feeding cakes of Russian manufacture, consisting of linseed-oil cake and a so-called starch cake. Of the nine samples he describes four as adulterated, two of medium quality, and three as good; the adulterations consist of the seeds of various weeds, and in some of the samples particles of straw. From these results the author urges the employment of the microscope, a botanical examination, treatment with warm water, and the judging of the samples by smell and taste. He agrees with Voelker, that an ordinary chemical analysis is not sufficient in such cases; he particularly recommends careful search for mildew in the centre of the cake. In some parts of Russia, it is the custom to stove the seeds previous to pressing them, in

order to get a better yield of oil, thereby injuring the quality of the cake, and probably forming matters injurious to the cattle which use it.

J. F.

**Spent Hops as Fodder.** By O. KELLNER (*Bied. Centr.*, 1879, 667).—A diet of hops and hay was daily given to two sheep, and afterwards for a short time hay alone, in order to ascertain the digestibility of the spent hops. The composition of the dried substance was as follows:—

|         | Protein. | Fibre. | Fat. | Nitrogen<br>free extract. | Ash and<br>sand. |
|---------|----------|--------|------|---------------------------|------------------|
| Hops .. | 19.7     | 21.7   | 7.8  | 46.1                      | 4.6              |
| Hay ..  | 8.7      | 34.5   | 2.7  | 45.2                      | 8.9              |

Of these constituents the animals digested—

| Hops.           | Organic<br>substance. | Protein. | Fibre. | Fat. | Nitrogen<br>free extract. |
|-----------------|-----------------------|----------|--------|------|---------------------------|
| Animal No. 1 .. | 28.6                  | 38.9     | —      | 77.2 | 43.2 per cent.            |
| „ No. 2 ..      | 37.7                  | 34.7     | 10.1   | 75.9 | 45.8 „                    |

HAY.

|                 |      |      |      |      |        |
|-----------------|------|------|------|------|--------|
| Mean of both .. | 59.4 | 52.7 | 54.5 | 48.6 | 65.0 „ |
|-----------------|------|------|------|------|--------|

The above numbers show that only a comparatively small percentage of the hop constituents was digested by the animals. Taking also into consideration the fact that the animals showed great objection to this food, spent hops cannot be highly recommended as fodder (comp. this Journal, 36, 1050).

J. K. C.

**Nitrogen in Turf.** By M. v. SIVERS (*Landw. Versuchs.-Stat.*, 24, 188—210).—The author comments at considerable length on the several results of 26 analyses of turf taken at different depths, and formed from various vegetable growths. The source of the nitrogen is attributed to the albuminoids of the decaying plants, the amount of these being sufficient to account for most of the nitrogen present, and they are not destroyed in the process of decay. The nitrogenous substances are soluble in potash.

J. K. C.

**On various Manures.** By J. MOSER (*Bied. Centr.*, 1879, 721—726).—As foreign manures are in general too high-priced in Austria, an investigation of various materials to be obtained in that country, both natural and artificial, which may be used as manure, has been made at the agricultural station in Vienna.

The beds of phosphorite examined, found chiefly in Idria and East Galicia, were not sufficiently rich to allow of being worked. The product obtained by treatment of sewage with lime was found to be valuable. Waste products from various manufacturing processes were also examined, such as fish-guano, dried blood, glue waste, &c., the results showing that they are very valuable as manures. Bat-guano, which occurs in very large quantities in some parts of Austria, proved on analysis to be a manure of excellent quality.

J. K. C.

**Manuring Experiments.** By F. BILCK (*Bied. Centr.*, 1879, 729—736).—In order to institute a comparison between cow and sheep dung in their influence on the growth of vegetables, a series of experiments was made in Silesia. Details of the effects on various plants are given, from which it appears generally that the application of cow-dung delays the ripening and reduces the yield, whilst sheep-dung has in most cases the opposite effect.

J. K. C.

**Composition of Fowls' Dung.** By A. PETERMANN (*Bied. Centr.*, 1879, 784).—The samples analysed were collected on dry sand, and mixed into a homogeneous mass with 10 per cent. of gypsum. The following results were obtained on analysis:—

|   |        |
|---|--------|
| Water .....                             | 11.76  |
| Organic matter and ammonium salts ..... | 24.59  |
| Mineral matter soluble in acids .....   | 34.54  |
| „ insoluble „ .....                     | 28.21  |
|   | <hr/>  |
|   | 100.00 |

J. K. C.

**Bat-guano from Various Sources.** By A. VÖLCKER (*Bied. Centr.*, 1879, 783—784).—This kind of guano occurs in large quantities in the Southern States, Jamaica, East India, &c.; the analysis showed great variations, the principal constituents ranging as follows:—moisture, 6.7 to 64; organic matter and ammonium salts, 5.8 to 65; phosphoric acid, from 1.4 to 24.9, and nitrogen from 0.3 to 8.9 per cent. in 21 samples.

J. K. C.

## Analytical Chemistry.

**Gasometric Methods.** By D. AMADIO and P. FIGUERA (*Gazzetta*, 9, 404—418).—In the centre of the Valle del Bove of Etna there is a small lake, called the Lago di Naftia or Lago dei Palici, formed by the streams from the hills with which it is surrounded, but which is occasionally quite dry after a hot and dry summer. At the bottom of this lake are three large openings and many smaller ones (about 40), from which gas constantly issues, so that the lake appears to be in a state of ebullition. As animals which by chance go to drink of the water, have been noticed to drop down dead, it is believed in the district that the water is poisonous. The authors therefore determined to examine it, and for this purpose collected samples of the water, and also of the gas issuing from one of the larger openings.

Before making the examination of the gases it seemed desirable to study the gasometric methods ordinarily employed, some of which the authors have modified, besides introducing new ones. A modification of Bunsen's apparatus for collecting the gases in water is described which entirely obviates any chance admixture with air. The 41 known gaseous substances, of which a table is given, were examined with

respect to their behaviour towards reagents, the details of which are fully described.

It was found that acetate of lead was blackened by hydrogen sulphide, selenide, telluride, and arsenide, and also by liquid hydrogen phosphide, but neither by phosphine nor by antimoniuiretted hydrogen. The four gases first named are absorbed by manganese peroxide, which moreover decomposes antimoniuiretted hydrogen with liberation of the hydrogen. Silver nitrate decomposes arseniuiretted, antimoniuiretted, and phosphoretted hydrogen, setting free hydrogen. A coke ball impregnated with ammonical chromous sulphate absorbs acetylene and allylene, but has no action on the gaseous olefines or paraffins. A coke ball with fuming sulphuric acid absorbs gases of the acetylene group as well as the olefines. The authors find also that a dry gas, when exploded with twice its volume of oxyhydrogen mixture, is completely saturated with aqueous vapour after the explosion.

Details are then given of the analysis of the gas collected from the openings (I), and from the water (II) with the following results:—

|                         | I.           | II.         |
|-------------------------|--------------|-------------|
| Carbonic anhydride..... | 94.23        | 84.58       |
| Hydrogen sulphide.....  | —            | 6.17        |
| Methane.....            | 1.82         | 2.42        |
| Oxygen.....             | 0.28         | 4.52        |
| Nitrogen.....           | 3.79         | 1.89        |
|                         | <hr/> 100.12 | <hr/> 99.58 |

Qualitative analysis showed that the gases were free from nitrogen oxides, arsenic, antimony, and the hydrocarbons of the acetylene and olefine series. The sudden death of the animals which had been observed must be referred therefore not to any poisonous effect of the water, but rather to the carbonic anhydride which constantly streams from the numerous openings, and in a calm atmosphere forms a stratum over the surface of the lake. C. E. G.

**Extension of Dietrich's Table for the Calculation of Nitrogen.** By E. TRACHSEL (*Zeits. Anal. Chem.*, 1880, 48).—This table gives the weight of a c.c. of nitrogen for temperatures varying from 5—25° C., and pressures from 705—720 mm. C. E. G.

**Determination of Carbonic Acid in Carbonates.** By G. W. WIGNER (*Analyst*, 1879, 228—230).—In the case of white lead, where the proportion of carbonic acid present is really the standard by which to judge of its suitability for use as a paint, the results obtained with the ordinary forms of carbonic acid apparatus are not of a satisfactory character. The only satisfactory process by which carbonic acid can be estimated in such samples is by measuring the volume of the gas evolved on treating the sample with dilute nitric or hydrochloric acid, and ascertaining that this gas is entirely carbonic acid. The author has for some time used an apparatus, in which the decomposition of the carbonates is entirely performed in a partial vacuum, so that the

liberation of the carbonic acid proceeds rapidly and freely at a temperature considerably below the ordinary boiling point of the solution. By this means the time necessary for the decomposition is greatly shortened, and the risk of the evolution of any other gases than carbonic acid is also decreased. Details of the apparatus required and the mode of treatment are given. D. B.

**Volumetric Estimation of Manganese and Cobalt.** By C. RÖSSLER (*Annalen*, 200, 323—340).—This is an investigation of certain points in connection with the author's method for the volumetric estimation of manganese (Abst., 1879, 746). The manganese is precipitated as a definite compound,  $\text{Ag}_2\text{O} \cdot \text{Mn}_2\text{O}_3$  (*Pogg. Ann.*, 41, 344, and 101, 229), by adding decinormal silver solution in excess followed by an alkali; the excess of silver is removed by ammonia and estimated by means of a standard thiocyanate. The author finds that the presence of ammonium salts at the time of precipitation has the effect of retaining a large proportion of the manganese in solution, and must therefore be carefully avoided. Accurate results are obtained by the following method:—The silver solution is added in excess to the manganese solution, the whole is then heated on the water-bath, and sodium carbonate is added in excess. The excess of silver above that required to form the compound with the manganese is removed by means of ammonia and estimated with thiocyanate. The presence of iron ( $\text{Fe}'''$ ) does not affect the results obtained.

It was ascertained by direct experiment that the compound  $\text{Ag}_2\text{O} \cdot \text{Mn}_2\text{O}_3$  gives up none of its silver to ammonia, provided this already contained silver in solution; this condition obtains in the above method.

*Applications of the Method.*—Where the nature of the substance permits, as in the case of iron (metal), spathic ore, and blast-furnace slags, nitric acid should be employed in effecting its solution. Manganese dioxide, in its several forms, is digested at a gentle heat with aqueous sulphurous acid; concentrated sulphurous acid is then added and the liquid boiled; lastly, the solution is oxidised with nitric acid. In cases where it is necessary to decompose with aqua regia, the solution must be boiled, after adding sulphuric acid, until the whole of the chlorine is expelled. Cast iron is dissolved in nitric acid and the iron precipitated as basic acetate in the usual way; this has the effect of entirely decolorising the solution by the removal of the carbonaceous matter, the presence of which in solution would prejudice the results.

*Estimation of Cobalt.*—This metal is also precipitated by silver nitrate in presence of alkali (H. Rose, *Pogg. Ann.*, 101, 498), and upon the formation of this compound the author has based a volumetric method for the estimation of cobalt, differing from that adopted in the case of manganese only in the substitution of alkaline hydrate for carbonate.

The method gives fairly accurate results in presence of nickel, provided the quantity of the latter does not exceed that of the cobalt. Perfect accuracy is attained by previously separating the metals by means of potassium nitrite. The precipitate may be dissolved in

nitric acid, without washing, and the cobalt estimated in the solution by the method described. C. F. C.

**Decomposition of Arsenic and Antimony Compounds.** By E. DONATH (*Zeits. Anal. Chem.*, 1880, 23).—The excellent method of fusing with sodium carbonate and sulphur sometimes gives doubtful results, owing to the large quantity of free sulphur separated from the aqueous solution before and on the addition of hydrochloric acid. This difficulty is avoided by using sodium thiosulphate (proposed for a similar process by Froehde), well dried and finely powdered, instead of the sulphur fusion mixture. J. T.

**Rapid and Easy Process for Simultaneously Detecting Nitrogen, Sulphur, and Chlorine in Organic Compounds.** By P. SPICA (*Gazzetta*, 9, 574—575).—The substance to be examined is heated with sodium in a test-tube, and the product dissolved in water, as in the ordinary way of testing for nitrogen by Lassaigne's process; the solution will then contain the nitrogen in the state of cyanide, the sulphur as sulphide, and the chlorine, bromine, or iodine as chloride, bromide, or iodide if these elements be present. A drop of the alkaline liquid placed on a clean silver surface will at once produce a black stain if a sulphide has been formed, whilst the cyanogen may be detected by the Prussian blue test in a portion of the liquid. If neither of these is present, the halogen may be at once tested for in another portion of the solution by adding nitric acid and silver nitrate, but if a sulphide or cyanide is present it must be first destroyed by mixing the solution with about half its bulk of pure sulphuric acid and heating for a short time before adding the silver nitrate.

C. E. G.

**Examination of the Will-Varrentrap Method of Nitrogen Determination.** By A. PREHN and R. HORNBERGER (*Landw. Versuchs.-Stat.*, 24, 21—34).—The doubts thrown upon the accuracy of the soda-lime process have induced the authors to make a series of experiments in order to verify the results of the Will-Varrentrap and Dumas systems, to ascertain the defects of the former, and to remedy them if possible. They considered that the first experiment should be as to the behaviour of free ammonia in the combustion-tube, for which purpose they employed salts of ammonia, and commenced the series with chemically pure sulphate,—the usual routine being followed, the ordinary precautions taken, and a dull red heat employed, the tube being arranged so as to be aspirated at the termination of the experiment. The results were too low by about  $1\frac{1}{2}$  per cent. The hinder end of the tube was then filled with soda-lime mixed with sugar, from which better results were obtained, but still below the theoretical numbers. In the next experiment the hinder end was fused to a round-shape, sugar and soda lime being placed at the opening; the tube was heated to expel the atmospheric air, and after the combustion, the other portion lying behind the substance ignited to clear the tube of gas. Notwithstanding all precautions, however, the results were too low, distillation with milk of lime yielding more exact numbers.

Similar results followed the employment of ammonium oxalate, the

theoretical numbers being never reached; the operations with this salt also succeeded better with sugar than without, and better results still were obtained when the sugar was not mixed with, but separated from, the substance. The low results point, in the authors' opinion, to some unexplained decomposition by which free nitrogen is lost, and think it proved that the Will-Varrentrap method is attended with danger of incorrect results when employed for estimation of certain salts of ammonia. They recommend distillation with milk of lime as a convenient and correct substitute. It was with ammonium chloride that the results looked for were first obtained.

In the first experiment with the chloride, sugar was not employed and air was sucked through; the results were low. Employing sugar to expel the gas *after* the operation, but not before, the results were better; but with sugar employed, both before and after the combustion of the substance, the whole theoretical amount was obtained. The same satisfactory result was obtained by connecting the tube with an easily regulated hydrogen apparatus to clear it before and after the combustion, which leads to the belief that a great dilution of the substance is not so important as a thorough expulsion of atmospheric air. With substances naturally poor in nitrogen the system would be successful, using only the ordinary precautions, probably because the gases given off, even at a gentle heat, would drive out the air and remove the oxygen, so that the loss of ammonia would either be very small or none. In fact, the objection to the method that it gives too low results applies only to substances rich in nitrogen; with matters containing small proportions the authors think the trustworthiness of the method incontestable.

Equally good results were obtained from potassium ferrocyanide, a substance for many reasons suitable for testing the method.

The remaining experiments were made to learn the effect of longer or shorter tubes and higher degrees of heat upon the combustion, and are explained in the tables accompanying the article, in which short tubes are held to mean those of 35–40 cm., and long those from 55–60 cm.; by ordinary heat is meant the usual dark red glow; high heat is the greatest obtainable from a gas-combustion furnace.

General recommendations of the authors are the careful expulsion of air *before* as well as of the gas *after* the combustion; not to employ the longer tubes where there is danger of excessive heat, but with ordinary heat good results may be obtained from long as well as short tubes; to proportion the amount of sugar to the richness of the substance in nitrogen, and to have the heat neither too strong nor too weak.

#### ABSTRACT OF TABLES.

##### *Ammonium Sulphate containing 21.21 per cent. N.*

|  | Found. |
|--|--------|
| Without sugar, aspirated, low temp., 5 experiments .....     | 19.61  |
| With sugar, without aspiration, low temp., 9 experiments.... | 20.67  |

##### *Ammonium Oxalate containing 19.71 per cent. N.*

|  |       |
|--|-------|
| Without sugar, aspirated, low temp., 3 experiments ..... | 19.14 |
|--|-------|



|   | Found. |
|---|--------|
| With sugar mixed with substance,* not aspirated, low temp., 7 experiments ..... | 19.03  |
| With sugar, not aspirated, low temp., 8 experiments .....                       | 19.59  |
| Do. do. high temp., 3 „ .....   | 19.54  |

*Ammonium Chloride containing 26.16 per cent. N.*

|  |       |
|--|-------|
| Without sugar, aspirated, low temp., 4 experiments .....                   | 24.97 |
| With sugar in fore part of tube, aspirated, low temp., 2 experiments ..... | 26.01 |
| With sugar in hinder part, not aspirated, low temp., 4 experiments .....   | 23.57 |
| With sugar before and behind substance, low temp., 6 experiments .....     | 26.12 |
| With sugar before and behind long tube, high temp., 5 experiments .....    | 23.54 |

*Potassium Ferrocyanide containing 19.87 per cent. N.*

|  |       |
|--|-------|
| Without sugar, aspirated, short tube, low temp., 2 experiments .....         | 19.50 |
| With sugar both extremities, short tube, low temp., 8 experiments .....      | 19.80 |
| With sugar both extremities, short tube, very low temp., 2 experiments ..... | 19.58 |
| With sugar both extremities, long tube, very low temp., 2 experiments .....  | 19.85 |
| With sugar both extremities, short tube, high temp., 10 experiments .....    | 19.36 |
| With sugar both extremities, long tube, high temp., 5 experiments .....      | 18.90 |

J. F.

**Estimation of Nitrogen in Albuminates.** By U. KREUSLER (*Landw. Versuchs.-Stat.*, 24, 35—40).—This paper is almost a continuation of that by Prehn and Hornberger (see preceding Abstract), and has also been called forth by the controversy on the respective merits of the Dumas and Will-Varrentrap methods of nitrogen estimation. The author in previous experiments has obtained very satisfactory results from the soda-lime process without the employment of any extraordinary precautions, and his experience makes him doubtful of the great value of sugar in a combustion. He, however, refers to some as yet unpublished experiments of the same chemists, Prehn and Hornberger, with the casein of milk, as proving more clearly the trustworthiness of the combustion with soda-lime process, and as proving the value of sugar. His experiments were instituted with a view of adapting the volumetric plan as a verification of the other system. His experiments were, he asserts, numerous and exhaustive, and from the experience gained he has become aware of sources of error in the Dumas process, not only such as are generally admitted, but others scarcely so well known. One of the worst is the presence of atmospheric

\* The only experiment in which sugar was mixed directly with the substance.

air in the carbonic acid gas, which is passed through the arrangement. He considers the gas as generally prepared to be unfit for the purpose, and advises employment of carbon dioxide obtained from sodium bicarbonate. A second he states to be the common neglect of repeated annealing of the copper reduced by hydrogen. Far more serious and more difficult to be avoided is the persistent adherence of particles of air to the walls of the tube, the copper oxide, and to the substance itself; he gives examples of the difficulty of its removal. The exhaustion of the tube by a Sprengel pump to  $\frac{1}{10}$  of an atmosphere does not seem to remove the air sufficiently to affect the result. The use of a larger quantity of material lessens the amount of the error, but gives rise to another, as the longer time required for the operation allows decompositions to take place, which vitiate the results. Another difficulty in the way of the use of the Dumas method is to prevent loss in the form of carburetted hydrogen. It is a common experience in elementary analysis that an unavoidable loss of carbon generally takes place, and when it is remembered that every equivalent of carbon which is consumed as marsh-gas equals  $2\frac{1}{2}$  equivalents of nitrogen in the estimation, it becomes a serious matter. The employment of mercury, leading to an intermittent passage of the gases, and a large quantity of copper oxide, is another source of error. The author recommends the use of asbestos copperised by steeping in a strong solution of copper nitrate and ignition. These errors, calculated to increase the nitrogen numbers in an analysis, are not compensated by others of a contrary nature, unless such arise from careless manipulation, which of course are as likely to be in one direction as the other. In the author's opinion, the method of Dumas cannot be accepted as a check upon the soda-lime process, as the errors of the two tend in opposite directions, even with the greatest precautions, and without great care, the small differences may amount to large discrepancies.

The author believes that both methods are in need of and capable of being perfected, and of yielding fairly satisfactory results.

J. F.

**Determination of Dry Substances by the Use of Alcohol.** By F. TSCHAPLOWITZ (*Landw. Versuchs.-Stat.*, 24, 47—48).—The author having been previously unsuccessful in obtaining a perfectly dry residue from apples by means of a stream of hydrogen, devised at last the following method, which gives satisfactory results:—A few small portions are cut from an apple, contained in a small weighed covered glass, with a sharp knife, which is wiped upon a dried and tared filter, afterwards used for the filtration. The slices are then treated in a small beaker with absolute alcohol, containing about 10 to 20 per cent. ethylic ether; and the liquid is repeatedly boiled and filtered into a 500—1,000 c.c. flask; the fragments of substance can then be easily broken into minute particles on the filter, and, with the aid of a small wash-bottle, transferred to the beaker and again boiled. Should an oil determination be desired, it can be readily made at this point, it being only necessary to employ more ether. The solid residue is dried at 100 to 110° with the filter; the filtrate in the flask is filled to the mark; 50 to 100 c.c. taken, dried in an air-bath, the heat of which at first should not exceed 60°, but which at the end of three or four days

may be raised to 85 or 90°, a higher temperature leading to decomposition. The author considers the results very satisfactory. J. F.

**Detection of Salicylic Acid in Wine and in Fruit Juices.** By L. WEIGERT (*Zeits. Anal. Chem.* 1880, 45) — Ferric chloride solution, the best reagent for salicylic acid, cannot be added directly to strongly coloured wines and fruit juices, as a coloured precipitate is formed. Previous decolorisation by means of animal charcoal also removes the greater part of the salicylic acid; 50 c.c. of wine and 5 c.c. of amyl alcohol are well shaken together for some minutes. After standing, the upper layer of amyl alcohol is removed and treated with an equal quantity of alcohol. To this solution some drops of dilute ferric chloride solution are added, when the characteristic deep violet coloration, if salicylic acid is present, is produced. J. T.

**Determination of the Fat in Milk by the Lactobutyrometer.** By F. SCHMIDT and Others (*Bied. Centr.*, 1879, 770—772).—The authors recommend the following modifications of Marchand's original method:—Non-addition of caustic soda, use of alcohol of 91 per cent. instead of 86, measuring the liquids in pipettes, and employment of other formulæ which they furnish. In answer to Marchand's defence of his original method, they bring forward the results obtained by the use of the modifications proposed. J. K. C.

**Quality of Milk.** By H. SCHULZE, R. FRÜHLING, and J. SCHULZ (*Bied. Centr.*, 1879, 780—782).—A controversy between the first-named and the two latter analysts has been going on with reference to the percentage of solids in milk, the former asserting that under some circumstances this percentage in unadulterated milk may fall under 10, and the latter refusing to acknowledge milk as genuine which contains less than 11 per cent. of total solids. J. K. C.

**Estimation of Albuminoids in Vegetable Substances.** By B. DEHMEL (*Landw. Versuchs.-Stat.*, 24, 214—225).—After giving some account of the methods already known for the determination of albumin, the author proceeds to recommend precipitation whilst hot with copper sulphate solution, adding potash until neutral, filtering, and estimating the nitrogen in the filtrate by heating with soda-lime. Asparagine was found under these circumstances to remain entirely in solution. Potatoes, however, appear to contain some other nitrogenous body, which is precipitated along with the albumin, as the results obtained by the author were much higher than those obtained by other investigators. J. K. C.

**New Method of Ascertaining the Ripeness of Grapes.** By E. POLLACCI (*Bied. Centr.*, 1879, 764—765).—The skins of unripe grapes contain two colouring matters, phylloxanthin, which is yellow, and phyllocyanin, which is green; the latter disappears when the grapes are ripe. To ascertain the absence of the latter body, the author treats the skins with dilute sulphuric acid, to dissolve out any red colouring matter, and removes the phylloxanthin with carbon bi-

sulphide. Treatment with ether will then extract the phyllocyanin, if any be present.

J. K. C.

**Examination of Coffee.** By A. H. ALLEN (*Analyst*, 1880, 1—4).—In 1874 the author described (*Chem. News*, 29, 140) three methods as likely to be of service for the approximate determination of chicory in samples of mixed coffee, viz.: (1) determination of the soluble ash; (2) comparison of the tint of an aqueous solution of the sample with that furnished by similarly treating a standard specimen; (3) determination of the density of a 10 per cent. infusion in hot water. Since the publication of these methods, the author has acquired a large amount of additional experience in their use, and has arrived at the following conclusions:—

With respect to method (1), experience has shown that it is only capable of furnishing results of the roughest possible kind. This fact is due to the variations in the percentage composition of the ash of both coffee and chicory, as well as to differences in its total amount. The differences shown by coffee are, however, exceeded by those exhibited by chicory, owing to the considerable and very variable proportion of silica present in the latter substance. This method can therefore be employed only as a check on the proportion of chicory in a mixture.

Method (2) is capable of giving rapid and fairly trustworthy estimations of the proportions of chicory present in mixed samples, but in practice it is open to the very serious objection that a standard mixture of various coffees and chicories is apt to undergo a change which gravely affects the colour of the infusion.

Method (3) is one which further experience has proved to be very valuable. The author has reason to think that exhaustion of the sample is usually tolerably perfect, but it is better to boil well, filter and wash the residue with hot water until the filtrate measures 10 c.c. for every gram of the sample operated on.

In sorting coffees for further examination, the author makes the following tests:—

(a.) Treatment of the sample with hot water and determination of the density of the 10 per cent. infusion, which should not exceed 1009. (b.) Search for starch in strained infusion, which should give negative results. (c.) Examination of the insoluble residue under the microscope. (d.) Determination of the ash, which ought not to exceed 5 per cent.

D. B.

**Analysis and Composition of English Beers.** By T. A. POOLEY (*Analyst*, 1880, 4—7).—The author has made analyses of various beers brewed in different parts of the kingdom under various systems and with a variety of materials, the object in view being to ascertain the exact proportions of all the more important constituents in the typical descriptions of beers brewed in this country, in order that a comparison may be made as to their respective values as foods and wholesome stimulants. No claim is made to any originality of method of analysis, for as a rule, the best methods as laid down by well known authorities on chemical analysis have been closely followed; but when

the exigency of the occasion required it, a modification has been introduced. The determinations usually made have been as follows:—Sp. gr., original gravity, carbonic acid, alcohol-extract, acetic acid, glucose, dextrin, lactic acid, ash including silica, lime, phosphoric acid and sodium chloride, nitrogen, and the corresponding quantity of albuminoid bodies. In the second part of this paper the author describes the method of analysis employed, and gives the results obtained with a sample of beer purchased from a public house in Messrs. Truman, Hanbury, and Co.'s trade. D. B.

**Adulteration of Bone-Meal.** By KROCKER (*Bied. Centr.*, 1879, 726—729).—It is usual in the manufacture of bone-meal to increase the percentage amount of nitrogen by the addition of horn and other nitrogenous bodies; the nitrogen contained in horn is, however, not so valuable as a manure as that present in bone-glue, and therefore the quality of the meal is reduced. The author proposes an easy method of detecting the presence of foreign nitrogenous substances in bone-meal, by the differences in specific gravity. The sp. gr. of bone-meal containing glue is 1.9, whilst that of dried blood and horn is about 1.3: if then we shake up a sample of meal with chloroform (sp. gr. 1.48) and allow it to settle, the blood, horn, and other impurities, will float on the liquid, and can be removed, and their amount roughly estimated. J. K. C.

**Behaviour of Fruit-Juices of Different Ages with Reagents.** By F. v. LEPEL (*Zeits. Anal. Chem.*, 1880, 24—44).—The juices examined were those of raspberry, wild strawberry, cherry, and red currant. Absorption-spectra were observed by means of a pocket spectroscope.

*Fresh Juice.*—There is nothing peculiar in the absorption-spectra of these juices to distinguish them from the juices of other red berries and fruits. Raspberry gives reactions with lead acetate, silver nitrate, ferric chloride, and manganic chloride. Cherry gives reactions with alum, lead acetate, ferric chloride, manganic chloride, and ether.

Wild strawberry gives reactions with caustic alkalis, lead acetate, alcohol, chloroform, and benzene.

Red currant gives reactions with aluminium acetate, lead nitrate. By means of these reactions mixtures of the juices can be examined; but a known mixture of the juices should be simultaneously examined.

The presence of sugar, and of hard water, if such have been used in preparing the juices, have no effect on these reactions. By adding very dilute alkaline solution to slightly acidified juice, an indefinite number of absorption-spectra can be obtained.

*Old Juice.*—In course of a year, raspberry juice changes in colour and in its reactions with metallic salts, so that coloured precipitates change in intensity of colouring (lead acetate) or in definiteness of colouring (copper sulphate), or precipitates obtained in fresh juice, fail altogether in the old (ferric chloride, uranium nitrate, and manganic chloride). Cherry juice is very stable. At the end of three years, metallic salts give almost the same reactions as with the fresh

juice, manganic chloride however gives no precipitate. Wild strawberry juice is much changed at the end of four years; and the characteristic reactions with chloroform or benzene only hold for very fresh juice. Red currant juice is very stable, and its colour is intense after four years. The reactions with metallic salts are almost the same as in the case of raspberry. All the juices in course of time give an absorption-spectrum cut off at the line G, and a more or less perceptible line in the orange. The absorption near E—F becomes less sharp towards D, and extends somewhat more in this direction.

The reactions with acids are the same with old as with new juices, but on careful addition of alkalis, the deep violet-blue colour, and in the case of strawberry, the deep orange-red colour, are not obtained; similarly by adding acid and carefully neutralising with alkali, the blue colour is not obtained.

As a general reagent, silver nitrate gives with old raspberry a blue fluorescence, and with the others a dirty green one, and with a large excess of the reagent reduced silver.

J. T.

**Determinations of Nitrogen in Explosive Ethereal Nitrates.** By TSCHELZAFF (*Ber.*, 12, 1486).—The author modifies Champion and Pellet's method (*Ber.*, 9, 1610) by conducting the decomposition in a stream of carbonic anhydride, and determining the ferric chloride formed, by adding stannous chloride in excess and titrating back with iodine.

Ch. B.

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## Technical Chemistry.

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**Oxidation of Sulphur in Gas on Combustion.** By W. C. YOUNG (*Analyst*, 1879, 201).—In a former communication the author published an account of some experiments, made for the purpose of ascertaining whether sulphurous or sulphuric acid was produced by the combustion of gas containing sulphur, the results of which led him to the conclusion that practically the whole of the sulphur present was at once converted into sulphuric acid. On absorbing the acid fumes by passing the products of combustion over zinc in a fine state of division, the author hoped to find a very simple method of estimating sulphur.

In practice it was found, however, that the zinc was quite unaffected except in places where moisture had condensed, and there sulphate had formed. It was noticed, moreover, that wherever sulphate was, there also was carbonate to be found. In investigating the subject further, the author determined to avoid using any alkaline or basic substance as an absorbent of the acid. Numerous experiments were made, the results showing beyond doubt that sulphurous acid only is formed when gas is burned in a Bunsen burner under the "gas referees" apparatus, as the small quantity condensed as sulphuric acid by water alone may reasonably be assumed to have been oxidised,

during its passage through the apparatus. In all the experiments where alkali or alkaline carbonate was used as the absorbent, no trace of the sulphite could be detected, the whole of it being oxidised to sulphate.

D. B.

**Norwegian Phosphorite.** By A. PETERMANN (*Bied. Centr.*, 1879, 783).—This is one of the richest phosphorites known to commerce, and contains 86 per cent. of calcium phosphate.

J. K. C.

**Preparation of Phosphorite.** By F. VORSTER (*Bied. Centr.*, 1879, 783).—To prevent the soluble phosphoric acid being rendered again insoluble by the iron and alumina present, the phosphorite is roasted with pyrites until the latter is quite decomposed: in this process the sulphur is oxidised to sulphurous and sulphuric acids, which in contact with calcium carbonate and iron phosphate, form calcium sulphate and a soluble phosphate, the iron and alumina being rendered insoluble.

J. K. C.

**Constitution and Properties of Dialysed Iron.** By M. PERSSONNE (*J. Pharm. Chim.* [4], 30, 332—334).—The liquid sold under this name is a pseudo-solution of modified ferric oxide, which differs from the ordinary oxide by having a less specific heat and being insoluble in acids. This modification of ferric oxide was discovered twenty-five years ago by Pean de St. Gilles, who obtained it by heating ferric acetate; subsequently Béchamp obtained it by heating ferric nitrate. The purest commercial sample of this liquid prepared by dialysis still contained 6.75 per cent. of ferric chloride, and 0.76 per cent. of ferric sulphate. Acids, strong or dilute, precipitate ferric oxide from this solution; the same effect is produced by solutions of salts. It is completely insoluble in gastric juice. A quantity of it was injected into the stomach of a dog during digestion, and after two hours the stomach was opened, when flocculent particles of ferric oxide were found adhering to the undigested food, whilst no trace could be found in solution in the acids of the stomach or along the surface of the alimentary canal. The author concludes that this substance is medicinally inactive, and that its commercial success at the present day, after having been abandoned for many years, is due to the manner in which it has been advertised.

J. M. H. M.

**Bessemer Steel Plates.** By S. KEEN (*Chem. News*, 40, 206).—For the rolling of boiler plates out of Bessemer ingots, it is preferable to use ingots hammered after casting. The reasons for doing so may be explained as follows:—

1. The plates obtained by the rolling of hammered ingots have a smooth, fine surface. Flaws, scale or excavations, are seldom observed, and, if present, must be attributed to imperfect rolling.

2. Plates from hammered ingots have a higher density, a good structure, and are more uniform in their mechanical qualities, such as tensile strength per square inch, elongation, &c. Such plates, even unannealed, will always stand the test within the limits of the Lloyd's regulations.

On the other hand, plates rolled directly out of unhammered ingots show much fluctuation in their mechanical properties. D. B.

**Comparison of Various Milk Coolers.** By WÜST (*Bied. Centr.*, 1879, 778—780).—The coolers examined were those of Lawrence, Rössler, and Neubecker. Of these, Rössler's appeared to combine the advantages of the other two as being applicable where cold water is obtainable only in small quantity or in an impure state.

J. K. C.

**Machines for Milk Churning.** By EUGLING and Others (*Bied. Centr.*, 1879, 772—778).—Lefeldt's and Winstrup's machines are highly recommended, as also the "separators" of Nielsen and de Laval. By means of these 90—96 per cent. of the butter can be separated in the course of an hour's working.

J. K. C.

**Analysis of two Ancient Samples of Butter.** By G. W. WIGNER and A. CHURCH (*Analyst*, 1880, 17—21).—The authors have examined a sample of Irish bog-butter, which cannot be traced with any certainty to a particular locality. There is no doubt, however, that it is a perfectly authentic specimen, probably 1000 years old. The following results were obtained:—Volatile fatty acids, calculated as butyric, 0·6 per cent.; soluble fatty acids, not volatile, 0·42 per cent.; insoluble fixed fatty acids, 99·48 per cent.; glycerol, minute traces. The insoluble fatty acids contained 9 per cent. oleic acid, and 91·0 per cent. stearic and palmitic acids.

The other sample of butter, which is much older, was taken some time ago from an Egyptian tomb. It dates from about 400 or 600 years before Christ. It was contained in a small alabaster vase, and had apparently been poured in while in a melted state. In appearance, colour, smell, and taste it corresponds closely with a sample of slightly rancid butter. Analysis shows that the sample has not undergone any notable decomposition.

D. B.

**Manoury's Method of Desugarising Molasses.** (*Bied. Centr.*, 1879, 768).—The lime, after being slaked by the addition of a little water, is added to the molasses along with a small quantity of sodium or potassium carbonate. The sugar-lime is then purified by addition of alcohol.

J. K. C.

**Changes Effected by Fermentation in the Nitrogenous Constituents of Sweet Mash.** By P. BEHREND and A. MORGEN (*Landw. Versuchs.-Stat.*, 24, 171—181).—More than half the nitrogen of sweet potato-mash exists in the form of albumin; on boiling and filtering, the filtrate is found to contain the amido-compounds along with a small quantity of peptone, and fermentation removes about one-fifth of these from solution, whilst the albumin present becomes increased. The acid amides are converted by fermentation into amido-acids, with formation of ammonia, which goes to nourish the yeast, whilst the amido-compounds as a whole are partially converted into albuminoid bodies, and thus the nutritive value of the mash is materially increased.

J. K. C.



**Influence of Varying Pressures on Grape-Must and Wine.** By C. WEIGELT (*Landw. Versuchs.-Stat.*, 24, 13—19).—The author having formerly made experiments on the aëration of the must, observed during their progress that the musts which run from the press at different stages of the pressure exhibited remarkably varying amounts of sugar, and he undertook his present series of experiments in order to ascertain if the separation of the juice obtained at different stages of the operation would improve the wine.

The experiments were made with 1 hectolitre of mash, containing berries in all stages of ripeness. The use of mashed grapes of course affected the results to a certain extent, but it was thought advisable to follow the custom of the country in its mode of wine manufacture. The press used was an ordinary iron arrangement, and operations were commenced some hours after the mashing had finished, but before fermentation had commenced. The juice from the press was divided into three portions—that which flowed without pressure; that obtained by slight hand pressure on the screw; and that which was obtained by the greatest amount of leverage obtainable on such an instrument.

The results of the experiments were contrary to the author's expectation, as the different portions showed an almost constant proportion of sugar, a slight diminution taking place at the second pressure.

The increase in tannin and colouring matter was constant, but so also was the decrease in acidity. The behaviour of the tartar was peculiar; that remaining in solution gradually increased, the deposited tartar, on the other hand, diminished with each accession of pressure; the sum of the two shows a regular increase, which, taken in connection with the decrease of acidity, convinces the author of the presence of a large amount of malic acid in the must taken for the experiment, which he considers surprising.

The practical results of the investigation were that it was undesirable, at least unprofitable, to separate the yield of the different pressures in a year of bad vintage, such as that in which the experiments were made; the author, however, hopes that he may be enabled to repeat his experiments on better fruit in a more favourable year, and compare the results.

J. F.

**Use of Thiocyanates in Calico Printing.** (*Dingl. polyt. J.*, 235, 156.)—These compounds serve as resists for aniline colours, as previously shown by Storck and Strobel, and they give a method for extracting the ammonium salt from gas liquors. The liquid is first slightly acidulated with hydrochloric acid, and after the effervescence has ceased, cuprous chloride, or a mixture of cupric chloride and sodium bisulphite is added to the clear liquid, and the grey precipitate of copper thiocyanate is collected. On treating with baryta-water, and concentrating, barium sulphocyanate is obtained in the crystalline state, and can easily be converted into other thiocyanates.

J. T.

**New Coal-tar Colours.** (*Dingl. polyt. J.*, 235, 154.)—Przibram and Co., in Vienna, have patented a method of preparing red, violet, and blue colours from mono- and diamido-anthraquinones, and rela-

tively from mono- and dinitro-anthraquinone. The amido-compounds are prepared by known methods, or better by one of the two following ones:—100 kilos. nitroanthraquinone, 2,000 kilos. water, and 300 kilos. ammonia solution are heated to boiling in a closed vessel, and tin-dust is added; after the reduction is ended, the liquid is filtered, and air is blown through the filtrate; the amido-compound thus precipitated is filtered off and washed. By the second method 100 kilos. anthraquinone (?) are heated with 300 kilos. concentrated ammonia solution, the excess of ammonia is blown off. 10 kilos. of mono- or diamido-anthraquinone are heated to 100° with 50 kilos. of sulphuric acid of 40 per cent. strength, until all quinone disappears; the mass is then thrown into water, sodium chloride added, the whole cooled, filtered, and washed. With stronger acid, less of it and a lower temperature are required; on the contrary, if the heating be continued too long, sulpho-compounds of the colours are produced. From monamido- or nitro-anthraquinone, red colours are thus produced, and from the diamido- or dinitro-anthraquinone, blue ones. According as a tin, aluminium, or chromium mordant is used, can shades from red to violet with the red colour be obtained, and shades from violet to blue with the blue colour. J. T.

**New Azo-colours.** (*Dingl. polyt. J.*, 235, 155.)—Meister, Lucius, and Brüning have patented a process for the production of a new series of azo-colours. The colours are obtained by the action of the two naphthalenedisulphonic acids on the diazo-compounds of phenol and naphthol, as well also on their corresponding methyl- and ethyl-ethers. To obtain the diazo-compounds of phenol the corresponding amidophenol is obtained from nitrophenol by reduction with zinc and hydrochloric acid, and the diazophenol is then produced by the action of nitrous acid. The nitrophenol ethers obtained from potassium nitrophenol, and ethyl or methyl bromide, serve as starting points for the preparation of the amidophenetols and amidoanisols; and these are converted into the corresponding diazophenol ethers as above. These diazo-compounds, treated with a solution of a  $\beta$ -naphthalenedisulphonic salt (see *Dingl. polyt. J.*, 232, 544), yield the azo-colours, which are sent into commerce as potassium or sodium salts. J. T.

**Soluble Essence of Ginger.** By J. C. THRESH (*Pharm. J. Trans.* [3], 10, 193).—To prepare an essence which does not become turbid by keeping, and which has not lost any appreciable quantity of the active principle of ginger during preparation, the author recommends the following process as an improvement on one previously suggested by him:—To 1 pint of strong tincture (1 to 1) of finest Jamaica ginger, slaked lime is added in a finely-powdered state in small quantities at a time. The addition is continued with vigorous agitation until the tincture ceases to lose colour; the whole is then thrown upon a filter, and the residue washed with proof-spirit until the filtrate measures two pints. Sulphuric acid is then added drop by drop until the rich yellow colour of the tincture suddenly disappears, and after standing for 24 hours, the liquid is filtered, diluted with water to four

pints, shaken with a little powdered pumice or silica, and filtered at  $0^{\circ}\text{C}$ ., if possible.

In this process, the lime removes the greater part of the resin, and the sulphuric acid removes the lime. The dilution with water separates the neutral resin, wax, fat, and peculiar extractive, and also the excess of volatile oil; the filtration at a low temperature prevents turbidity from separation of essential oil. The pale colour of the essence can be changed to rich orange by addition of a few drops of potash.

F. C.

**Mineral Constituents of Cinnamon and Cassia.** By O. HENNER (*Analyst*, 1879, 225—228).—The discrimination between ground cinnamon and cassia being a matter of some importance, but of considerable difficulty, the author determined to investigate this subject more minutely. The only test which has been in use is that founded on the alleged difference in the behaviour of the decoctions towards iodine; but the fact is that decoctions of both cassia and the cheaper kinds of genuine cinnamon turn blue with iodine.

To find, if possible, some real difference between the two kinds of bark, the author examined their mineral constituents, believing that the more woody bark, cassia, would contain a larger amount of salts of lime and magnesia than the delicate membranous cinnamon. The following analyses show, however, that this supposition was not entirely substantiated. An analysis was made upon the ash obtained at the lowest possible temperature, but not recarbonated:—

|                                 | Coal. | Sand. | SiO <sub>2</sub> . | CO <sub>2</sub> . | P <sub>2</sub> O <sub>5</sub> . |
|---------------------------------|-------|-------|--------------------|-------------------|---------------------------------|
| (1.) Cinnamon, 1s. 10d. per lb. | 0.27  | 1.09  | 0.27               | 29.29             | 3.52                            |
| (2.) „ 3s. „                    | 0.41  | 0.53  | 0.31               | 32.27             | 2.20                            |
| (3.) „ 3s. 6d. „                | 0.31  | 0.52  | 0.25               | 32.40             | 3.00                            |
| (4.) Cassia lignea .....        | 1.26  | 3.16  | 0.90               | 27.18             | 3.67                            |
| (5.) „ vera .....               | —     | 0.24  | 0.20               | 36.26             | 1.13                            |

|                                 | SO <sub>3</sub> . | Cl.  | Fe <sub>2</sub> O <sub>3</sub> . | Mn <sub>2</sub> O <sub>4</sub> . | CaO.  |
|---------------------------------|-------------------|------|----------------------------------|----------------------------------|-------|
| (1.) Cinnamon, 1s. 10d. per lb. | 2.42              | 0.18 | 0.78                             | 0.86                             | 40.09 |
| (2.) „ 3s. „                    | 2.73              | 0.51 | 0.41                             | 0.97                             | 36.98 |
| (3.) „ 3s. 6d. „                | 2.84              | 0.76 | 0.46                             | 0.13                             | 40.39 |
| (4.) Cassia lignea .....        | 2.02              | 0.14 | 1.23                             | 5.11                             | 25.29 |
| (5.) „ vera .....               | 0.71              | 0.09 | 0.14                             | 1.13                             | 52.72 |

|                               | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. | Totals. | Ash. |
|-------------------------------|------|-------------------|--------------------|---------|------|
| (1.) Cinnamon, 1s 10d per lb. | 2.65 | 14.22             | 3.98 =             | 99.62   | 4.78 |
| (2.) „ 3s. „                  | 3.30 | 16.70             | 2.97 =             | 100.29  | 4.59 |
| (3.) „ 3s. 6d. „              | 3.86 | 10.35             | 4.65 =             | 99.92   | 4.66 |
| (4.) Cassia lignea .....      | 5.48 | 20.58             | 3.98 =             | 100.00  | 1.84 |
| (5.) „ vera .....             | 1.10 | 5.60              | 0.90 =             | 100.16  | 4.08 |

D. B.

## General and Physical Chemistry.

**Spectroscopic Researches.** By G. L. CIAMICIAN (*Wien. Akad. Ber.* [2], 79, 8—10).—By passing induction sparks from a small coil, connected with a weak battery, between electrodes made of the metals of the earths contained in tubes filled with hydrogen, the author obtained calcium and strontium spectra which had an extraordinary resemblance to the spectrum of magnesium. These spectra appeared also to contain the lines of the less refrangible half of the oxygen spectrum. The author thinks that his observations support the view which regards the so-called elements in each natural group as really compounds containing some common principles. R. R.

**A New Chemical Photometer.** By J. M. EDER (*Ber.*, 13, 166—168).—A solution of mercuric chloride is decomposed by exposure to sunlight. The presence of certain organic compounds greatly facilitates the reduction.

In order to make use of this reaction in estimating the chemical activity of light, a mixture is prepared which consists of 2 volumes of a solution of 40 grams of ammonium oxalate in 1 litre of water, and 1 volume of mercuric chloride solution (50 grams per litre). The liquid is exposed to the light until it becomes slightly turbid; it is then filtered, and may be preserved in the dark without undergoing any change.

The red, yellow, and yellowish-green light have no action on this solution; nine-tenths of the mercurous chloride reduced by exposure to ordinary daylight is due to the action of the ultra-violet rays.

Since the quantity of mercurous chloride precipitated increases with the temperature and with the concentration of the reagent, corrections must be made for these variations.

The intensity of the light is expressed by the number of milligrams of mercurous chloride precipitated for each square centimetre of the surface of the liquid exposed to the light. W. C. W.

**Heat of Formation of Cuprous chloride (*sic*).** By J. THOMSEN (*Ber.*, 13, 138—139).—A reply to Berthelot's statement that the heat evolved in the formation of an aqueous solution of cupric chloride by the action of chlorine and water on cuprous chloride is equal to 54,200 c. (this vol., 208), and not 59,625 as found by the author (*J. pr. Chem.* [2], 12, 281). W. C. W.

**Heat of Formation of Cyanogen.** By J. THOMSEN (*Ber.*, 13, 152).—The author points out that the first determination of the heat of formation of cyanogen was made by Dulong (*Pogg. Ann.*, 92, 55). W. C. W.

**On the Carbonates.** By J. THOMSEN (*J. pr. Chem.* [2], 21, 33—45).—The heat of solution of carbonic anhydride, and the evolution of heat during its neutralisation by soda, have been described in a former  
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paper (*Pogg. Ann.*, **140**, 516). The present paper gives an account of experiments on the heat of neutralisation of carbonic anhydride for other bases, *i.e.*, of the heat of formation of the carbonates of barium, strontium, calcium, manganese, cadmium, lead, and silver.

The decomposition in the case of the barium salt is instantaneous, and the precipitate is amorphous and anhydrous. In the case of strontium, the precipitate is at first amorphous, but a further *evolution* of heat takes place as it becomes crystalline. Calcium carbonate is also at first amorphous, but the change to the crystalline state is accompanied by *absorption* of heat.

The following tables give the results obtained:—

(1.) An aqueous solution of carbonic anhydride acting on an aqueous solution of oxides and hydrates. (2.) Gaseous carbonic anhydride on anhydrous oxides.

| (1) R.                                | R + CO <sub>2</sub> Aq. | (2) RO.                | (RO + CO <sub>2</sub> ). |
|---------------------------------------|-------------------------|------------------------|--------------------------|
| Na <sub>2</sub> O.Aq. ....            | 20180 heat-units        | BaO ....               | 55580 units              |
| BaO.Aq. ....                          | 21820 "                 | SrO ....               | 53230 "                  |
| SrO.Aq. ....                          | 20550 "                 | CaO ....               | 52490 "                  |
| CaO.Aq. ....                          | 18510 "                 | PbO ....               | 22580 "                  |
| MnO <sub>2</sub> H <sub>2</sub> ..... | 13280 "                 | Ag <sub>2</sub> O .... | 20060 "                  |
| CdO <sub>2</sub> H <sub>2</sub> ..... | 12990 "                 |                        |                          |
| PbO .....                             | 16700 "                 |                        |                          |
| Ag <sub>2</sub> O .....               | 14180 "                 |                        |                          |

(3.) Evolution of heat during formation of anhydrous carbonates

(a) from metal, oxygen, and carbonic anhydride; (b) from metal, oxygen, and carbonic oxide.

| R.                    | (R + O + CO <sub>2</sub> ) | (R + O <sub>2</sub> + CO) |
|-----------------------|----------------------------|---------------------------|
| K <sub>2</sub> .....  | 184130 units               | 250940 units              |
| Na <sub>2</sub> ..... | 175680 "                   | 242490 "                  |
| Ba.....               | 185960 "                   | 252770 "                  |
| Sr.....               | 184210 "                   | 251020 "                  |
| Ca.....               | 173850 "                   | 240660 "                  |
| Mn.....               | 113880 "                   | 180690 "                  |
| Cd.....               | 84550 "                    | 151360 "                  |
| Pb.....               | 72880 "                    | 139690 "                  |
| Ag <sub>2</sub> ..... | 25960 "                    | 92770 "                   |

The following table shows the difference between the evolution of heat during formation of sulphates or nitrates and of carbonates:—

| R.                   | (R + O <sub>2</sub> + SO <sub>2</sub> ) -<br>(R + O <sub>2</sub> + CO.) | (R + O <sub>2</sub> + CO) -<br>(R + O <sub>2</sub> + N <sub>2</sub> O <sub>4</sub> ) |
|----------------------|---|--|
| K <sub>2</sub> ....  | 22620 units   | 7980 units   |
| Na <sub>2</sub> .... | 15020 "   | 15990 "  |
| Ba ....              | 13720 "   | 23020 "  |
| Sr ....              | 8800 "  | 27160 "  |
| Ca ....              | 8310 "  | 33420 "  |
| Pb ....              | 5440 "  | 30180 "  |
| Ag <sub>2</sub> .... | 3430 "  | 31290 "  |
| Cd ....              | -1150 "   | —  |
| Mn ....              | -1900 "   | —  |

The great difference between the heat of formation of the carbonates and the corresponding nitrates and sulphates would indicate a difference in constitution between the former and the latter.

G. T. A.

**Thermo-chemical Researches.** By J. THOMSEN (*J. pr. Chem.* [2], 46—76).—In this article the author gives a summary in seventeen tables of his thermo-chemical researches which have been published at various times in the *Annalen* and *J. pr. Chem.* As translations or abstracts of these tables have appeared from time to time in this Journal, it is unnecessary to give more than a list of the tables and their contents.

Tables 1, 2, 3 contain the heats of formation and solution of the anhydrous and hydrated compounds of chlorine, bromine, and iodine.

4. The heat of formation of various hydracids of the haloid metals.

5. Heat of formation of the oxides and their hydrates.

6. Heat of formation of sulphides and sulphhydrates.

7. Heat of neutralisation of bases for sulphuric, hydrochloric, nitric, and acetic acids.

8. Evolution of heat in the reaction of gaseous hydracids on anhydrous oxides.

9. Evolution of heat during the formation of sulphates of the formula  $R.O_2.SO_2.nH_2O$ , and their heat of solution.

10. Evolution of heat during the formation of anhydrous nitrates from their elements.

11. Evolution of heat during the formation of nitrates of the formula  $R.O_2.N_2O_4.nH_2O$ , and their heat of solution.

12. Evolution of heat during the formation of sulphates and nitrates in aqueous solution, of formula  $R + O + QAq$ .

13. Heat of formation and solution of the dithionates.

14. Heat of formation of carbonates.

15. Heat of formation and solution of some double salts.

16. Evolution of heat during decomposition of metallic salts by sulphuretted hydrogen.

17. Energy of various galvanic combinations.

G. T. A.

### Condensation of a Liquid at the Wet Surface of a Solid.

By A. SCHLEIERMACHER (*Dingl. polyt. J.*, 234, 471).—For the determination of the standard weights, numerous investigations have been carried out regarding the weight of the unity by volume, viz., water. These investigations, although made with great care, showed that the value of a kilo. had been determined with a probable error of  $\pm 76$  mgrms. All determinations which give the value of the kilo. are derived from hydrostatic weighings of accurately measured bodies. It is known, however, that the state of a liquid is different at a limiting surface from what it is in the interior of the liquid. Whilst the particles in the interior of the liquid are influenced to the same extent on all sides, those in contact with a solid surface are simultaneously exposed to the action emanating from that surface. If the attraction of the solid particles surpasses that existing between the liquid ones, a

layer of condensed liquid will be formed at the surface of the solid body, the weight of which has hitherto not been considered.

From the accounts respecting the determination of the new English standard pound, the author calculates the value of the coefficients of condensation for water on brass at  $\beta = 0.00092$  g. sq. c. The separate values of the kilo. are freed from the influence of surface-condensation by adding to each one of them the corresponding correction  $\frac{1}{2}\beta$ . This is more fully illustrated by the following table:—

|               | Shape.   | Volume. | Surface. | $\frac{o}{v}$ | Value of<br>1 kilo. | Corrected. |
|---------------|----------|---------|----------|---------------|---------------------|------------|
|               |          | c.c.    | sq. cm.  |               | g.                  | g.         |
| England ..... | cube     | 2046    | 968      | 0.478         | +0.555              | +0.990     |
| " .....       | sphere   | 1850    | 729      | 0.394         | +0.555              | +0.917     |
| " .....       | cylinder | 1234    | 618      | 0.526         | +0.334              | +0.817     |
| France .....  | "        | 11264   | 2784     | 0.247         | $\pm 0.000$         | +0.227     |
| Sweden .....  | "        | 1234    | 618      | 0.526         | +0.296              | +0.779     |
| Austria ..... | "        | 387     | 294      | 0.760         | -0.348              | +0.350     |
| Russia .....  | "        | 822     | 486      | 0.592         | -0.065              | +0.478     |
| " .....       | "        | 402     | 301      | 0.750         | +0.041              | +0.729     |
| Average ..    | —        | —       | —        | —             | +0.171              | +0.661     |

The author shows that the thickness of the condensed layer for water and glass does not amount to 0.001 mm. D. B.

**Diffusion of Liquids.** By J. STEFAN (*Wien. Akad. Ber.*, 78 [2], 957—975, and *ibid.*, 79 [2], 161—214).—In these papers, the author enters into a full mathematical discussion of the numerical results which have been obtained in the principal experimental researches into the diffusion of soluble substances through their liquid solvents. Fick (*Pogg. Ann.*, 94, 59) had pointed out that the formulæ of the propagation of heat in solid conductors were applicable to diffusion phenomena; the formula, which is the starting point of the discussion, is therefore

$$S = kqt \frac{u_1 - u_2}{l},$$

where  $S$  represents the quantity of salt which has passed through the section  $q$  in the time  $t$  between horizontal strata, the concentration of which is represented by  $u_1$  and  $u_2$  respectively, and their distance by  $l$ ;  $k$  is a coefficient, depending only on the nature of the salt and of its solvent.

The first paper relates to investigations conducted by optical methods; those, namely, in which the concentration of the various horizontal layers is inferred from the refractive power, or in the case of saccharine solutions, from the polarising power. The researches chiefly discussed are those of Voit (*Pogg. Ann.*, 130, 227) and of Hoppe-Seyler (*Medicinisch-chemische Untersuchungen*, I, Berlin, 1866)

on sugar solutions; and those of Johannisjanz (*Wiedemann's Annalen*, 2, 24) and of Fick, on saline solutions. The author's conclusion from the results of the discussion is, that the optical methods of investigation are wholly untrustworthy. Not only are they liable to extraordinary errors, but their inaccuracy may, in certain cases, be concealed by an apparently tolerable agreement of the results with each other and with the theoretical formulæ, whilst these results may, nevertheless, be very far from the truth. The author describes some experiments of his own to prove that rays of light passing through a solution wherein diffusion is proceeding do not retain their horizontality; and he remarks that this fact may also be deduced from the known laws of refraction.

The second paper is occupied by a minute discussion of Graham's researches on liquid diffusion (*Phil. Trans.* for 1861, 138—224; *Phil. Mag.* [4], 33, 204—233, 290—306, 368—380). The original paper should be consulted for the results of the mathematical discussion of the several series of Graham's experiments, as these do not well admit of abstraction. The general conclusion, however, is, that Graham's results do show a satisfactory, and in some relations a remarkably close, agreement with theory.

R. R.

**Some Chemical Constants.** By J. V. JANOVSKY (*Wien. Akad. Ber.*, 78 [2], 1004—1012).—If by *quantivalence* we understand the *maximum* capacity of saturation of an atom or of a molecule, the quantivalence will then have a constant value, and it will be the quotient which results from dividing the atomic weight by the equivalent. Also, the quantivalence of carbon compounds will be equal to the sum of the quantivalences of the several constituent elements, *plus* a constant. These laws are illustrated and discussed at large in the paper.

R. R.

**Limits and Velocities of Chemical Reactions.** By A. POTILITZIN (*Ber.*, 12, 2371—2374).—The mutual reaction of bodies depends on the atomic weights (which are related to the energy of the atomic motion) and on the mass (the number of impacts in the unit of time). Reactions are therefore independent of the direction of the heat-change produced by the reaction, the speed of the reaction only being influenced by the absorption or evolution of heat. A reaction between two bodies present in equivalent quantities proceeds up to a certain limit, which depends on the occurrence of a state of unstable equilibrium between two opposite reactions. Heat-change accelerates the motion of the molecules and atoms, and therefore causes the limit to be attained more quickly. The commencement of a reaction depends on the ratio of the masses of the acting bodies to the velocity of the molecular motion. If this be true, the necessity of a preliminary heat-change, whether of absorption or of evolution, is fully accounted for.

T. C.

**Mutual Replacement of the Halogens.** By A. POTILITZIN (*Ber.*, 12, 2369—2371).—A continuation of the author's previous work on this subject (*ibid.*, 9, 1027; this Journal, 1877, ii, 109).—Bro-



mine displaces chlorine from the anhydrous metallic chlorides, and if the bodies be present in equivalent quantities, then the percentage of chlorine displaced depends on the atomic weight of the metal, and the atomicity of the latter in such a way that

$$\frac{A}{pE^2} = \text{constant.}$$

Where  $A$  = atomic weight,  $p$  = percentage of chlorine displaced, and  $E$  = the atomicity of the metal. The following table contains the results obtained, and from these the above rule was deduced:—

| RCl.     |     |       |               |                  |
|----------|-----|-------|---------------|------------------|
|          | A.  | p.    | $\frac{A}{p}$ | $\frac{A}{pE^2}$ |
| Li.....  | 7   | 1.84  | 3.80          | 3.80             |
| Na ..... | 23  | 5.56  | 4.13          | 4.13             |
| K.....   | 39  | 9.78  | 4.00          | 4.00             |
| Ag ..... | 108 | 27.28 | 3.98          | 3.98             |

| RCl <sub>2</sub> . |     |       |               |                  |
|--------------------|-----|-------|---------------|------------------|
|                    | A.  | p.    | $\frac{A}{p}$ | $\frac{A}{pE^2}$ |
| Ca .....           | 40  | 2.5   | 16.0          | 4.0              |
| Sr .....           | 87  | 5.21  | 16.7          | 4.2              |
| Ba .....           | 137 | 7.78  | 17.6          | 4.4              |
| Hg .....           | 200 | 12.02 | 16.6          | 4.2              |
| Pb .....           | 207 | 12.43 | 16.6          | 4.1              |

| RCl <sub>3</sub> . |     |      |               |                  |
|--------------------|-----|------|---------------|------------------|
|                    | A.  | p.   | $\frac{A}{p}$ | $\frac{A}{pE^2}$ |
| Bi .....           | 208 | 5.38 | 38.66         | 4.3              |

| RCl <sub>4</sub> . |     |      |               |                  |
|--------------------|-----|------|---------------|------------------|
|                    | A.  | p.   | $\frac{A}{p}$ | $\frac{A}{pE^2}$ |
| Sn .....           | 118 | 1.49 | 79.19         | 4.9              |

| R <sub>2</sub> Cl <sub>6</sub> . |     |      |               |                  |
|----------------------------------|-----|------|---------------|------------------|
|                                  | A.  | p.   | $\frac{A}{p}$ | $\frac{A}{pE^2}$ |
| Fe <sub>2</sub> .....            | 112 | 0.72 | 155.5         | 4.3              |

T. C.

**Lecture Experiment.** By H. SCHULZE (*Ber.*, 13, 44—45).—This is a description of a simple apparatus to show the liquefaction of such a gas as ethyl chloride, and consists of a tube closed at one end by a stopcock, and connected at the other by means of a stout caoutchouc tube with a reservoir containing mercury, which may be raised or lowered.

P. P. B.

## Inorganic Chemistry.

**Non-existence of Pentathionic Acid.** By W. SPRING (*Annalen*, 201, 377—380).—A reply to Kessler's remarks (*Annalen*, 200, 256; this vol., 298) on the author's research on this subject (*Annalen*, 199, 97—115; and this vol., 215). W. C. W.

**Phosphoric Acid.** By W. F. HORN (*Pharm. J. Trans.* [3], 10, 468—469).—Phosphoric acid may be readily prepared by covering a stick of vitreous phosphorus with water, adding a crystal or two of iodine and some nitric acid, and allowing the mixture to stand for 24—36 hours. After the oxidation is complete, the solution is evaporated and treated as the Pharmacopœia directs. The advantages presented by this method are economy of material, and consequent safety, and the indefinitely large quantities of phosphorus which can be oxidised by a very small quantity of iodine. The theory of the process is based on the discovery of Brodie (this Journal, 1852, 289) that the iodine converts the vitreous phosphorus into the amorphous variety, which is oxidised by the nitric acid. This method differs from that of Pettenkoffer, who treats phosphorus iodide with water, and obtains phosphorous acid, which is oxidised by nitric acid.

L. T. O'S.

**Sodium Hypophosphite.** By BOYMOND (*Pharm. J. Trans.* [3], 10, 407—408).—Pure sodium hypophosphite may be prepared by treating 25 grams commercial sodium hypophosphite (containing phosphite) and 1 gram barium hypophosphite with water, and making the volume up to 50 c.c. After some time, 200 c.c. of absolute alcohol are added, the mixture allowed to stand, and then filtered from the barium phosphite and hypophosphite. The last traces of barium are removed from the solution by adding the requisite quantity of sodium sulphate and 100 c.c. absolute alcohol, and decanting the clear solution, which is mixed with 500 c.c. absolute alcohol and sufficient absolute ether to allow of the mass being well agitated. Sodium hypophosphite is thus completely separated, and, after being collected, is dried in a current of air. Thus prepared, the salt is entirely free from phosphite, which is always present when the usual methods are employed.

L. T. O'S.

**Ultramarine Compounds.** By K. HEUMANN (*Annalen*, 201, 262—291).—The results of the experiments on the decomposition of silver ultramarine (from ultramarine blue) by dilute hydrochloric and nitric acids and by solutions of sodium chloride and soda (*Ber.*, 12, 60, and this Journal, 1879, Abst., 437) show that in this compound one-third of the silver is present as sulphide and two-thirds as aluminium-silver silicate. On fusion with potassium iodide, the silver ultramarine is converted into potassium ultramarine (*Ber.*, 12, 784, this Journal, 1879, Abst., 692). By a similar reaction, *lithium ultramarine* can be prepared. It has a beautiful blue colour, and resembles the corresponding potassium and sodium compounds in its properties.

When heated with sulphur in a current of air, its colour changes to green, and finally to pink. A red compound is obtained by heating the blue lithium ultramarine in a current of hydrochloric acid and air, but its colour is changed to blue by exposure to sulphur vapour or hydrogen.

By long-continued digestion with an ammoniacal solution of silver chloride, blue sodium ultramarine is converted into a yellow compound, in which two-thirds of the sodium in the ultramarine have been replaced by silver. On exposure to hydrochloric acid gas, this product turns blue.

The silver can be replaced by an alkali by fusion with an alkaline iodide.

By the action of silver nitrate on green ultramarine at  $120^{\circ}$ , a yellow compound is obtained which bears a strong resemblance to the ordinary silver ultramarine, but differs from it in yielding a green product on fusion with potassium iodide. W. C. W.

**Spontaneous Oxidation of Manganese Oxides with reference to the Manganese Recovery Process.** By J. Post (*Ber.*, 13, 53—56).—The author finds that when a solution of manganese chloride is treated with lime water in excess, and a current of oxygen passed through the solution, it gradually becomes less alkaline, the manganese being oxidised at the same time. This he regards as explained by the formation in the first place of a manganese oxychloride, which is oxidised, with liberation of hydrochloric acid, the latter uniting with the alkalis. The existence of an oxychloride is supported by the fact that the precipitate formed by adding an alkali to manganese chloride contains chlorine, and is decomposed by washing and exposure to the air. This formation of an oxychloride the author thinks explains the formation of the "red charge" in the Weldon process, which takes place when an insufficiency of lime is added. The "red charge" after washing is found to contain no chlorine. In this case the oxygen expels the chlorine from the molecule as hydrochloric acid, and enters it to form a species of anhydride: the hydrochloric acid so liberated reacts with an oxide of manganese to form manganous chloride. The formation of this latter body has been demonstrated by experiment.

The formation of the "thick charge" takes place in the Weldon process when too much lime is added and the blast of air is not strong enough. This phenomenon is due to the formation of calcium oxychloride; for when calcium chloride solution is mixed with twice the quantity of slaked lime, and then heated to  $60^{\circ}$ , a thick mass is produced consisting of crystals of calcium oxychloride.

P. P. B.

**Composition of Weldon Mud and Similar Compounds.** By J. Post (*Ber.*, 13, 50—53).—The author gives some analyses of unheated and but slightly washed Weldon mud, which bear out his conclusion (*Ber.* 12, 1454) that the quantity of lime present is smaller than is required to form a compound with manganese dioxide. Further, that the compound described by Rammelsberg as  $(\text{MnO}_2)_2\text{K}_2\text{O}$  (*Ber.*, 8, 232), and obtained by heating potassium manganate, yields

after washing much less potash than is necessary for the above formula. The author concludes that the existence of a manganous acid is doubtful.

P. P. B.

## Mineralogical Chemistry.

**The Meteorite of Albarello.** By P. MAISEN (*Gazzetta*, 10, 20).—This meteorite, which fell at Albarello in July, 1766, has been analysed by the author with the following results:—

| Fe.   | Ni.   | Co.   | S.    | SiO <sub>2</sub> . | FeO.               | Al <sub>2</sub> O <sub>3</sub> . | MgO.       | CaO.  |
|-------|-------|-------|-------|--------------------|--------------------|----------------------------------|------------|-------|
| 4.332 | 0.730 | 0.105 | 2.364 | 35.913             | 24.313             | 4.479                            | 22.773     | 2.073 |
|       |       |       |       | K <sub>2</sub> O.  | Na <sub>2</sub> O. | Loss.                            | Mn and Cr. |       |
|       |       |       |       | 0.440              | 1.637              | 0.840                            | traces.    |       |

The silicate soluble in hydrochloric acid appeared to be analogous to olivine, and the insoluble silicate to bronzite.

C. E. G.

**Niobite from the Isergebirge.** By J. V. JANOVSKY (*Ber.*, 13, 139—142).—The following minerals are found in the Iser- and Riesengebirge. I. Niobite, a combination of  $\infty P_{\infty}$ ,  $\infty P_{\infty} . P . O P . \infty P_2 . \infty P_2$ ; sp. gr. 5.74. II. Iserite, sp. gr. 4.52,  $P . P_{\infty} . \infty P . \infty P_{\infty}$ , cleavage  $\infty P_{\infty}$ . III. Iserine, sp. gr. 4.742, magnetic; and IV. Zircon,  $\infty P_{\infty} . P$  and  $\infty P_{\infty} . mP . mPn$ ; sp. gr. 4.627—4.635:—

|                                      | I.    | II.   | III.  | IV.   |
|--------------------------------------|-------|-------|-------|-------|
| Nb <sub>2</sub> O <sub>5</sub> ..... | 62.64 | 0.44  | —     | —     |
| Ta <sub>2</sub> O <sub>5</sub> ..... | 16.25 | —     | —     | —     |
| TiO <sub>2</sub> .....               | —     | 68.99 | 38.84 | —     |
| FeO .....                            | 13.06 | 28.57 | 29.81 | —     |
| Fe <sub>2</sub> O <sub>3</sub> ..... | —     | —     | 27.35 | 0.53  |
| MnO .....                            | 6.11  | 1.41  | 3.33  | trace |
| ZrO .....                            | 0.48  | 0.00  | —     | 65.01 |
| SnO <sub>2</sub> .....               | 0.41  | —     | —     | 0.54  |
| WO <sub>3</sub> .....                | 1.01  | —     | —     | —     |
| H <sub>2</sub> O .....               | 0.34  | —     | —     | —     |
| MgO .....                            | —     | 0.32  | 1.15  | —     |
| SiO <sub>2</sub> .....               | —     | —     | —     | 33.63 |

The following numbers show the composition of red and blue spinelle:—

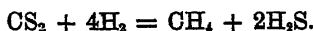
|                                      | Red.  | Blue.  |
|--------------------------------------|-------|--------|
| Al <sub>2</sub> O <sub>3</sub> ..... | 71.37 | 71.05  |
| CrO <sub>3</sub> .....               | 1.34  | —      |
| MgO .....                            | 27.11 | 25.97  |
| FeO .....                            | 0.25  | 3.36   |
| MnO .....                            | —     | trace. |

W. C. W.

## Organic Chemistry.

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**Action of Phosphonium Iodide on Carbon Bisulphide.** By H. JAHN (*Ber.*, 13, 127—135).—A new synthesis of methane is accomplished when a mixture of phosphonium iodide and carbon bisulphide is heated at 120—140° in a sealed tube from which the air has been expelled by carbonic anhydride or carbon bisulphide vapour. A red crystalline deposit is formed, and on opening the tube phosphoretted hydrogen, marsh gas, and sulphuretted hydrogen are evolved:—



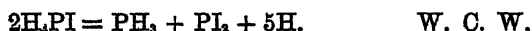
Baeyer (*Annalen*, 155, 266) ascribes the formula PI to the red crystalline compound, but it really appears to be a complex molecular compound of carbon bisulphide and phosphorus di-iodide, since it is decomposed by water, with liberation of sulphuretted hydrogen, and with formation of hypophosphorous and hydriodic acids, and of a white solid compound having the composition  $\text{C}_5\text{S}_7\text{P}_2\text{H}_4\text{O}_{12}$ .



This substance is also produced by the action of alcohol on the red crystals. When heated in sealed tubes with water free from air, it is decomposed according to the equation:—



It appears that when phosphonium iodide acts on carbon bisulphide, phosphoretted hydrogen, phosphorus di-iodide, and hydrogen are produced.



**Reactions due to the Presence of Aluminium Bromide and Chloride.** By G. GUSTAVSON (*Ber.*, 13, 157—159).—The author claims priority in reference to Kekule's explanation (*Ber.*, 12, 2280) of the conversion of propyl bromide into isopropyl bromide by aluminium bromide, viz., that the aluminium bromide forms addition-products with non-saturated hydrocarbons. W. C. W.

**Constitution of Diallyl.** By W. SOROKIN (*Ber.*, 12, 2374).—Diallyl, on oxidation with potassium permanganate, gives chiefly succinic acid, from which its constitution would appear to be represented by the formula  $\text{CH}_2 : \text{CH}.\text{CH}_2.\text{CH}_2.\text{CH} : \text{CH}_2$ . T. C.

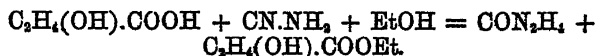
**Cyanamide.** By G. PRÄTORIUS-SEIDLER (*J pr. Chem.* [2], 21, 129; see this vol., 307).—(I.) The author has investigated the reaction of cyanamide with the following compounds:—

*Hydroxylamine Hydrochloride.*—The reagents were heated, in alcoholic solution, on the water-bath. After removing the ammonium chloride which had been formed, as platinochloride, the filtrate from the latter, containing excess of platinum chloride, yielded on spontaneous evaporation ruby-red prisms of a platinochloride

$(\text{CN}_2\text{H}_5\text{O.HCl})_2.\text{PtCl}_4$ , i.e., oxyguanidine platinochloride. Cyanamide and ammonium chloride react under similar conditions (Erlenmeyer, *Annalen*, 146, 258) to form guanidine, in complete analogy, therefore, to the present case. It was attempted, but without success, to isolate a simpler compound of the base, viz.:—(1) by precipitating the platinum of the platinochloride in alcoholic solution as sulphide, filtering and evaporating; (2) by the action of cyanamide on hydroxylamine sulphate in both aqueous and alcoholic solutions; and (3) by the action of cyanamide on hydroxylamine itself. In the two latter cases no decomposition occurred.

*Formic acid* was found to react with cyanamide according to the equation  $\text{H.COOH} + \text{CN.NH}_2 = \text{CO} + \text{CO}(\text{NH}_2)_2$ , cyanamide playing the part of a dehydrating agent.

*Lactic acid* decomposes cyanamide, in alcoholic solution also, with formation of urea, probably according to the equation—



*Phenol* was heated with a solution of cyanamide (in anhydrous alcohol); the result was a polymerisation of the latter, dicyanodiamide being formed.

*Salicylic acid* reacts with cyanamide in presence of alcohol, according to the equation:—



The isomeric hydroxybenzoic acids were without action on cyanamide, even under pressure.

*Thiacetic acid* reacts energetically with cyanamide, forming thiocarbamide and acetylthiocarbamide.

(II.) The author further contributes the following to the chemistry of thiocarbamide. That obtained as the product of the last-mentioned reaction was observed to melt in the first instance at  $170^\circ$ ; but, on again heating, it melted at  $149^\circ$ , the latter being the melting point observed by Reynolds (*Annalen*, 150, 220); thiocarbamide prepared from ammonium thiocyanate gives the same result:  $149^\circ$  is therefore the permanent, although not the original melting point.

*Platinochlorides*.—A mixture of saturated solutions of platinum chloride and thiocarbamide yielded microscopic red prisms of the compound  $\text{PtCl}_2(\text{CSH}_4\text{N}_2)_2.\text{HCl}$ , as stated and described by Reynolds (*ibid.*). The filtrate from this salt yielded on evaporation yellowish prisms of a new platinochloride,  $(\text{CSH}_4\text{N}_2.\text{HCl})_2.\text{PtCl}_4$ . This compound is soluble in water and in alcohol; it resists a temperature of  $100^\circ$ , but cannot be fused without decomposition. The author attempted to prepare the compound  $\text{PtCl}_2.\text{CSH}_4\text{N}_2$ , but without success. The corresponding aurochloride was prepared according to Reynolds' directions.

*Cuprosulphate*.—On mixing together concentrated solutions of thiocarbamide and cupric sulphate and leaving the solution to evaporate spontaneously, colourless prisms of the compound  $(\text{CSH}_4\text{N}_2)_2.\text{CuSO}_4$

are obtained. On heating the aqueous solution of this salt, it is decomposed with separation of copper sulphide.

*Thalliosulphate*.—The double salt,  $\text{CSH}_4\text{N}_2\cdot\text{TlSO}_4$ , was prepared in a similar manner. It is only slightly soluble in water and in alcohol. The aqueous solution may be boiled without decomposition; the salt melts at  $140\text{--}145^\circ$ , but not without decomposition. C. F. C.

**Normal Propyl Alcohol from Glycerol.** By A. FITZ (*Ber.*, 13, 36).—Amongst the fermentation-products of glycerol, the author, besides ethyl and normal butyl alcohol, has also obtained propyl alcohol. It boils at  $95\text{--}100^\circ$ , and the form of the barium salt of the acid obtained by its oxidation corresponds with that of barium propionate. P. P. B.

**Allylmethylpropyl Carbinol.** By SEMLIANIZIN (*Ber.*, 12, 2375).—This compound, prepared from allyl iodide, zinc, and methyl-propyl ketone, is a mobile colourless liquid (b. p.  $160^\circ$ ; bar. = 743 mm.), smelling somewhat of camphor. It is optically inactive, combines energetically with bromine, and is insoluble in water. Its sp. gr. at  $0^\circ = 0.8486$ ; at  $20^\circ = 0.8345$ ; and its coefficient of expansion between  $0^\circ$  and  $20^\circ = 0.00084$  for  $1^\circ$ . On oxidation with chromic mixture, it is converted almost wholly into carbonic anhydride.

*$\beta$ -Methylpropylethylactic acid*,  $\text{CMeH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained by oxidising the preceding compound with potassium permanganate. It is a thick syrup. The silver, calcium, and barium salts are described. T. C.

**Methyl and Ethyl Ethers of Diallyl Carbinol.** By RJABININ (*Ber.*, 12, 2374—2375).—These compounds are obtained by the action of methyl iodide and ethyl iodide respectively on the sodium compound of diallyl carbinol. Both are mobile liquids, of peculiar odour. The *methyl ether* boils at  $136^\circ$  (bar. 763 mm.); its sp. gr. is 0.8258 at  $0^\circ$ , and 0.8096 at  $20^\circ$ ; therefore, its coefficient of expansion between  $0$  and  $20^\circ$  is 0.0010 for  $1^\circ$ . The *ethyl ether* boils at  $144^\circ$  (bar. 759 mm.); its sp. gr. is 0.8218 at  $0^\circ$ , and 0.8023 at  $20^\circ$ ; and therefore its coefficient of expansion between  $0^\circ$  and  $20^\circ = 0.00121$  for  $1^\circ$ . Both ethers, on oxidation with chromic mixture, are converted almost entirely into carbonic anhydride. On oxidation with potassium permanganate, the methyl ether gives

*$\beta$ -Methoxyglutaric acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{COOH}$ , as a syrupy liquid, which after some time becomes partly crystalline. The calcium, barium, and silver salts are described. T. C.

**Composition of Pyroxylin.** By J. M. EDER (*Ber.*, 13, 169—186).—After referring to the researches of Hadow (*J. pr. Chem.*, 68, 51; 58, 15), Béchamp, Wolfram (*Dingl. polyt. J.*, 1878, 230), and many others, the author describes the properties of five cellulose nitrates.

*Cellulose hexanitrate*,  $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{NO}_3)_6$ , is prepared by immersing dry cotton wool in a mixture of 3 volumes of sulphuric acid (sp. gr. 1.845) and 1 volume of nitric acid (sp. gr. 1.5) at a temperature of  $10^\circ$  for 24

hours. The product is thoroughly washed with cold and finally with hot water. 100 parts of cotton yield from 175 to 180 of pyroxylin. A small quantity of oxalic acid and other organic compounds remain in the nitrosulphuric acid. The gun-cotton contains from 1.2 to 5.8 per cent. of penta- and tetra-nitrate, which may be removed by repeated digestion with a mixture of ether and alcohol (3 : 1).

The hexnitrate is insoluble in ether, alcohol, acetic acid, methyl alcohol, ether-alcohol, and ethyl acetate.

With acetone it forms a transparent jelly, which dissolves in a large excess of the solvent.

Thoroughly washed gun-cotton may be heated at 100° for several days without undergoing any change; its temperature of ignition is between 169° and 170°. Attempts to prepare the hexnitrate by treating the cotton with nitre and sulphuric acid did not yield satisfactory results.

*Cellulose pentanitate*,  $C_{12}H_{18}O_6(NO_3)_5$ , is formed, together with the tetranitrate, by digesting cotton wool for five hours at the ordinary temperature in a mixture of equal volumes of strong sulphuric and nitric (sp. gr. 1.4) acids. The product is washed and treated with ether to which a small quantity of alcohol has been added; in a few days a gelatinous mass is obtained which is poured into three times its volume of alcohol, when the pentanitate separates out, leaving the lower nitrates in solution.

The pentanitate can also be obtained by dissolving collodion-cotton in nitric acid (sp. gr. 1.4) at 60°; the turbid solution is cooled down to 0°, filtered through asbestos, and the filtrate is mixed with four times its volume of sulphuric acid (sp. gr. 1.84), care being taken to prevent the temperature of the mixture rising. The acid liquid is largely diluted with water and the precipitated pentanitate collected on a filter and purified by solution in alcoholic ether and reprecipitation by water.

This compound is insoluble in alcohol and in ether, but dissolves in ether-alcohol, in acetic acid, and in ethyl acetate.

The solution in alcoholic ether leaves on evaporation a transparent film; potash converts it into the dinitrate.

*Cellulose tetra- and tri-nitrates*,  $C_{12}H_{18}O_6(NO_3)_4$  and  $C_{12}H_{17}O_7(NO_3)_3$ , have not yet been obtained in the pure state. The tetranitrate is insoluble in alcohol and in ether, but dissolves in methyl alcohol, ethyl acetate, alcoholic ether, and in a mixture of acetic acid and alcohol or acetic acid and ether. The trinitrate dissolves freely in ethyl acetate, methyl alcohol, and boiling acetic acid. It is slowly dissolved by absolute alcohol, and the solution becomes turbid on the addition of ether in excess.

*Cellulose dinitrate*,  $C_{12}H_{13}O_8(NO_3)_2$ , is formed by the action of ammonia or potash on the higher nitrates. It is also prepared by adding alcoholic potash to collodion; the product is diluted with water and the aqueous solution neutralised with acetic acid, when the dinitrate is precipitated. After being dissolved in alcoholic ether, it forms a yellowish-white powder which explodes at 175°. It is soluble in alcoholic ether, absolute alcohol, methyl alcohol, acetic acid, ethyl acetate, acetone, and also in potash, but in the latter case a considerable por-



tion of the substance is decomposed. The solution in alcoholic ether deposits an opaque film on evaporation. The dinitrate appears to form compounds with alkalis which are insoluble in alcoholic ether, but dissolve in water.

The cellulose mononitrate could not be obtained.

In order to estimate the nitrogen in these compounds the following method was employed:—

0.2–0.3 gram of the substance are brought into a flask of 150 c.c. capacity, closed by a cork through which passes a tube bent twice at right angles. To this tube a piece of caoutchouc is attached so that the opening may be closed by means of a pinchcock. The flask, which is half filled with water, is heated until the air is completely expelled and only a small quantity of water remains in the flask. The end of the tube is now placed in a concentrated solution of ferrous sulphate in hydrochloric acid and the source of heat removed from the flask. The solution of ferrous salt is allowed to flow into the flask until it is one-third full, when the tube is closed by the pinchcock. A small quantity of water is afterwards admitted into the flask in order to wash the iron out of the tube, but care must be taken to avoid the entrance of air. The apparatus is heated and the nitric oxide is collected in a graduated cylinder filled with a strong solution of soda. The number of cubic centimeters of gas at 0° and 760 mm. multiplied by 0.62693 gives the milligrams of nitrogen, and multiplied by 1.72649 gives the milligrams of nitrogen tetroxide,  $N_2O_4$ .  
W. C. W.

**Synthetical Formation of Formic Acid.** By V. MERZ and J. TIBIRICA (*Ber.*, 13, 23–33).—The authors have investigated the conditions under which the formation of formic acid takes place by the action of carbonic oxide on caustic alkalis. They find that the absorption of this gas by alkalis with production of formic acid takes place at about 200°. In order to saturate the soda completely, it is best to use it as soda-lime, which must be porous. Another essential is that the carbonic oxide must be moist, and further, that the temperature must not be raised above 220°. Above this temperature the formate is decomposed into carbonate and hydrogen. With caustic potash or potash-lime, this secondary decomposition takes place below 220°, and more easily than with soda or soda-lime. Since the absorption of carbonic oxide by soda-lime, when the necessary precautions are taken, takes place very rapidly, the authors think that formic acid might be made on the large scale in this manner.

Experiments made in the hope of obtaining benzoic acid from sodium phenylate and carbonic oxide yielded negative results. Sodium ethylate absorbs carbonic oxide at 200°. The investigation of the products of this reaction is as yet unfinished.  
P. P. B.

**Maleic and Malic Acids from  $\alpha$ -Dibromopropionic Acid.** By S. TANATER (*Ber.*, 13, 159–161).—A mixture of maleic and malic acids is formed when a solution of  $\alpha$ -dibromopropionic acid is boiled for six hours with potassium cyanide and an excess of potash. The acids are obtained from the alkaline solution by acidification with hydrochloric acid and extraction with ether, and may be separated

by precipitating the maleic acid with barium acetate, when the malic acid will be found in the filtrate.

The barium and calcium malates are crystalline and dissolve readily in water. The silver salt is also soluble; the lead salt is insoluble in excess of lead acetate and does not melt in boiling water. The acid crystallises in needles (m. p. 100°), which are freely soluble in alcohol, ether, and water. In many respects it appears to resemble the isomalic acid prepared by Schmöger from isosuccinic acid. W. C. W.

**Etherification of Unsaturated Monobasic Acids.** By N. MENSCHUTKIN (*Ber.*, 13, 162—163).—The initial rate of etherification of the unsaturated monobasic acids is greatest for the primary and lowest for the tertiary acids, so that in this respect the non-saturated acids resemble the saturated.

| Primary unsaturated acids:                    | Initial rate. | Limit of etherification. |
|---|---------------|--------------------------|
| Hydrosorbic acid, $C_6H_{10}O_2$ .....        | 43.0          | 70.83                    |
| Phenylacetic acid, $C_6H_5CH_2COOH$ .....     | 48.82         | 73.87                    |
| Phenylpropionic acid, $C_6H_5(CH_2)_2COOH$ .. | 40.26         | 72.02                    |
| Secondary acids:                              |               |                          |
| Crotonic acid, $CH_3CH=CHCOOH$ .....          | 12.12         | 72.12                    |
| Cinnamic acid, $C_6H_5CH=CHCOOH$ .....        | 11.55         | 74.61                    |
| Tertiary acids:                               |               |                          |
| Sorbic acid, $C_6H_8O_2$ .....                | 7.96          | 74.72                    |
| Benzoic acid, $Ph.CO_2H$ .....                | 8.62          | 72.57                    |
| Paratoluic acid, $C_6H_4Me.CO_2H$ .....       | 6.64          | 76.52                    |
| Cumic acid, $C_6H_4(C_2H_5).CO_2H$ .....      | 6.26          | 75.91                    |

W. C. W.

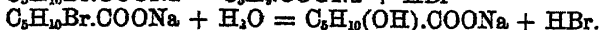
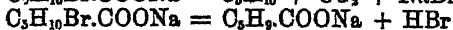
**Unsaturated Monobasic Acids with Six Atoms of Carbon.** By R. FITTIG and others (*Annalen*, 200, 21—65).—*Ethylcrotonic Acid*.—In preparing ethylic diethoxalate by the action of amalgamated zinc and ethyl iodide on ethyl oxalate (Frankland and Duppa, *Annalen*, 136, 2) the author recommends that the zinc should be only slightly amalgamated by a very brief immersion in a dilute solution of mercuric chloride. The ethylic ethylcrotonate obtained from this by the action of phosphorus chloride (for small quantities preferably by Geuther and Wackenroder's method with hydrochloric acid (*Zeit. Chem.*, 3, 709) need not be separated, but may be at once saponified by potash, the ethylcrotonic acid set free by acidifying the solution being distilled off with steam.

Ethylcrotonic acid is not attacked by nascent hydrogen from sodium amalgam, and combines but slowly with hydrobromic acid. To bring about this combination the acid must be saturated at 0° and used in large excess (200 c.c. to 10 grams). On standing for some weeks the addition product,  $C_6H_{11}BrO_2$ , separates from the mixture as a reddish oil, which solidifies when cooled to 0°, and may be dried over sulphuric acid and potash (m. p. 25°). When this addition-product is treated

with sodium-amalgam, under suitable conditions (*Annalen*, 195, 117), it is converted into a saturated acid,  $C_8H_{12}O_2$  (b. p. 194—195°). This is a colourless oily liquid, which is volatile with steam. Barium and calcium salts were prepared and analysed; the latter,  $(C_8H_{11}O_2)_2Ca + H_2O$ , is less soluble in hot than in cold water. The ethyl salt,  $C_8H_{11}O_2Et$  (b. p. 151.5°), is obtained by dissolving the acid in twice its volume of absolute alcohol, and heating this solution with an equal volume of sulphuric acid on the water-bath for half an hour. On dilution, the salt separates.

If the formula of ethylcrotonic acid is  $CH_3CH:OEt.COOH$ , the saturated acid derived from it is probably diethylacetic acid. An acid of this composition has been prepared by Frankland and Duppa (*Annalen*, 138, 221) by the action of sodium and ethyl iodide on ethyl acetate; by Schnapp (*Ber.*, 10, 1953) by heating  $\alpha$ -diethyl- $\beta$ -hydroxybutyric acid; and by Saytzeff (*Annalen*, 193, 349), from the cyanide corresponding with diethylcarbinol; but since this new acid does not agree in all points with the description of these chemists, the authors name it *hyloethylcrotonic acid*.

A solution of sodium carbonate at once decomposes bromhydroethylcrotonic acid into hydrobromic acid, carbonic acid, and amylene. The reaction must be conducted at 0°, as otherwise the amylene is almost entirely carried off by the escaping carbonic anhydride. This amylene is identical with the hydrocarbon *ethylpropylene* (b. p. 36°) obtained by Wagner and Saytzeff (*Annalen*, 175, 373; 179, 302) by treating the iodide from diethylcarbinol with alcoholic potash, and by Wurtz from allyl iodide and zinc ethyl, but has a higher boiling point than other known amylenes (Wischnegradski, *Ber.*, 9, 1028; *Annalen*, 190, 328; Le Bel, *Bull. Soc. Chim.*, 25, 546; *Compt. rend.*, 85, 853; Zeidler, *Annalen*, 186, 245; 197, 243; Eltekoff, *Ber.*, 10, 706, 1904, 2057; 11, 414; Flawitzky, *Annalen*, 169, 205; 179, 340; *Ber.*, 11, 992; Etard, *Compt. rend.*, 86, 488). A little ethylcrotonic acid is also produced in the reaction together with a third acid of doubtful composition. Heating the acid with five times its weight of water at 100° effects a similar decomposition, but in this case a relatively large quantity of ethylcrotonic acid and a little hydroxycaproic acid are also formed. As in the case of bromhydrocinnamic acid (*Annalen*, 195, 135), therefore, three reactions occur:—



A solution of ethylcrotonic acid in carbon bisulphide rapidly absorbs bromine, and on evaporation dibromethylcrotonic acid,  $C_8H_8Br_2.COOH$ , remains in large crystals (m. p. 80.5°). This acid also is decomposed by a cooled solution of sodium carbonate, or by digestion with water at 100° for 24 hours. In both cases, *bromamylene*,  $C_8H_8Br$ , is the principal product; in the latter, on evaporating the water and shaking with ether, an acid,  $C_8H_{12}O_4$ , named by the authors *hexenic acid*, is obtained in small colourless rhombic prisms which have been accurately measured (m. p. 141°). Hexenic acid is probably a homo-

logue of glyceric acid; its salts are uncrystallisable and exceedingly soluble in water.

*Hydrosorbic and Sorbic Acids.*—Hydrosorbic acid (*Annalen*, 161, 309) dissolves with evolution of heat in a solution of hydrobromic acid saturated at  $0^{\circ}$ , and after a few hours *monobromocaproic acid*,  $C_6H_{11}BrO_2$ , separates. When washed and dried, it forms a feebly odorous, colourless oil, which does not become solid at  $-18^{\circ}$ , and decomposes on distillation. In an analogous way *moniodocaproic acid*,  $C_6H_{11}IO_2$ , may be obtained as a colourless oil which turns yellow on exposure to light.

When sorbic acid is shaken with concentrated hydrobromic acid for some days, a light oil, doubtless *monobromohydrosorbic acid*, at first separates, but after a time becomes heavier, sinks and crystallises, being converted into  *dibromocaproic acid*,  $C_6H_{10}Br_2O_2$ , which is deposited from carbon bisulphide or benzene in large clear compact crystals (m. p.  $68^{\circ}$ ).

*Isodibromocaproic acid* has been prepared by Fittig and Barringer by the action of bromine on hydrosorbic acid in a freezing mixture; the two substances may also be brought together in solution in carbon bisulphide. It forms a thick uncrystallisable syrup, which decomposes slowly in the cold, rapidly at  $50^{\circ}$ .

Fuming hydriodic acid dissolves sorbic acid, and after some time an oily body is deposited, whilst much iodine is set free. The oily body is *moniodocaproic acid*,  $C_6H_{11}IO_2$ : the sorbic acid is therefore first reduced to hydrosorbic acid, which is then converted into the iodo-acid. Diiodocaproic acid could not be prepared.

When sodium amalgam is added in small quantities to a very dilute solution of monobromocaproic acid, the caustic soda formed being repeatedly neutralised with sulphuric acid, it yields a mixture of hydrosorbic and normal caproic acids, the latter of which has been described by Lieben and Rossi (*Annalen*, 159, 75), b. p.  $204.5^{\circ}$ ; m. p.  $-2^{\circ}$  (Freund, *J. pr. Chem.*, N.F., 3, 232). This experiment proves that the addition-compounds of sorbic and hydrosorbic acids must all be derivatives of normal caproic acid.

Boiling water or a dilute solution of sodium carbonate rapidly dissolves monobromocaproic acid: part of the acid is decomposed into hydrobromic and hydrosorbic acids, whilst another portion is converted into *hydroxycaproic acid*,  $C_6H_{11}(OH)O_2$ . The former having been removed by distillation with steam, the latter may be extracted by ether, from which it is deposited on evaporation as a brown-yellow syrup. Its salts are uncrystallisable and very soluble in water and alcohol. A solution of the free acid on spontaneous evaporation appears to leave an anhydride, which only redissolves on the addition of much water. In this behaviour the acid resembles lactic acid. It is not identical either with lencio acid or with the hydroxycaproic acid of Erlenmeyer (*Ber.*, 9, 1840), and Ley (*ibid.*, 10, 231), prepared from normal caproic acid.

*Dibromocaproic acid* is decomposed by heating with water at  $100^{\circ}$ , or by warming with sodium carbonate, yielding sorbic acid and a syrupy acid which is not volatile with steam. Isodibromocaproic acid, on the other hand, is only partially decomposed by prolonged heating with water, yielding two acids, both volatile with steam. One of these is sorbic acid, the other probably bromhydrosorbic acid. These having

been removed by distillation, the residue gave up to ether a liquid non-volatile acid. Analysis of a crystalline calcium salt of the acid showed that it was probably a *hydroxy-hydrosorbate*,  $(C_6H_6O_3)_2Ca + 1\frac{1}{2}H_2O$ . Evidently the isodibromocaproic acid is first resolved into hydrobromic and bromhydrosorbic acids: the latter is then decomposed partly into sorbic acid, partly into hydroxyhydrosorbic acid.

Tetrabromocaproic acid (the addition-product of sorbic acid) is very slowly attacked by water. It yields sorbic and brominated acids, together with an indifferent oil containing bromine. These products were not examined.

*Pyroterebic acid* is immediately dissolved by fuming hydrobromic acid with evolution of heat. On diluting and distilling, a neutral oily body passes over into the distillate, from which it may be separated by saturation with potassium carbonate. This body is isomeric with pyroterebic acid, and is the *internal anhydride* of *hydroxyisocaproic acid*,

$C_6H_{10}$   
 $\begin{array}{c} | \\ CO-O \end{array}$  (b. p. 206°), bearing to that acid the same relationship that

terebic bears to diaterebic acid (*Ber.*, 7, 649; *Annalen*, 180, 66). With the possible exception of the amidotrimethylbutyllactide of Heintz (*Annalen*, 189, 231; 192, 329 and 339), it is the first representative of its class in the lactic series. For this class of anhydrides the author proposes the name "lactones;" and as examples of lactones in other series, he instances paraconic, terebic, aconic, and muconic acids, the lactones of itamalic, diaterebic, hydroxyitaconic, and hydroxyhydromuconic acids, respectively.

Amongst aromatic bodies, umbelliferone, the phthalide of Hessert, Zincke's orthobenzhydrylbenzoic anhydride, Wreden's oxycamphic anhydride, and santonin, are also lactones. It is to be noted that the experiments of Henry (*Ber.*, 7, 753) have proved that lactide is not a lactone, as commonly assumed, but is really an anhydride derived from *two* molecules of lactic acid. The neutral reaction and solubility of the lactones of the lactic series are probably the cause of their having been hitherto overlooked. Like other bodies of its class, the lactone of hydroxyisocaproic acid yields a salt of that acid when boiled with alkalis. In its formation from pyroterebic acid, an addition-product of that acid with hydrobromic acid is probably first formed, viz., bromisocaproic acid, which immediately exchanges bromine for OH: the hydroxy-acid then passes into an anhydride. The intermediate bromisocaproic acid may be formed by saturating pure pyroterebic acid with dry gaseous hydrobromic acid, and exposing it to the air for some time: colourless crystals then separate in small quantity. These may be recrystallised from carbon bisulphide. Cold water does not dissolve them; but they are quickly decomposed by warm water. The acid was not analysed.

Ch. B.

**Methacrylic Acid.** By F. ENGELHORN (*Annalen*, 200, 65—74).—This acid gradually combines with hydriodic acid (*Annalen*, 188, 59), but not so easily with hydrobromic acid. Much of the acid becomes polymerised, unless it is treated with five times its volume of hydrobromic acid and the mixture allowed to stand surrounded by ice. On

diluting, a small quantity of oily condensation-products separates, and from the residue carbon bisulphide extracts a colourless oil which may remain long without solidifying. This the author names  $\beta$ -bromoisobutyric acid (m. p.  $22^\circ$ ) to distinguish it from ordinary or  $\alpha$ -bromoisobutyric acid (m. p.  $45^\circ$ ). Only two isomerides are theoretically possible: the  $\alpha$ -acid is with certainty  $\text{CH}_3\text{CMeBr.COOH}$ ; the  $\beta$ -acid must therefore be  $\text{CH}_2\text{Br.CHMe.COOH}$ . The iodobutyric acid previously obtained also belongs to the  $\beta$ -series, since its melting point ( $36^\circ$ ) is lower than that of the  $\alpha$ -bromo-acid, whereas it would be higher were they of similar constitution.

Unlike the  $\alpha$ -acid (Markownikoff, *Annalen*, 153, 228),  $\beta$ -bromoisobutyric acid does not yield a hydroxy-acid when boiled with barium hydrate, but breaks up into hydrobromic and methacrylic acids. Moreover the conversion of the  $\alpha$ -acid into hydroxy-acid is never complete; in one experiment only 54 per cent. of it underwent this change, the remainder yielding methacrylic acid. Hydroxybutyric acid is formed in large quantity when sodium carbonate is substituted for barium hydrate.

Methacrylic acid becomes polymerised by distillation (*Annalen*, 188, 47), by long keeping, by the action of acids, and when its aqueous solution is heated at  $130^\circ$ . The product in the latter case is a white porcelain-like mass, insoluble in all neutral menstrua, but swelling up like gum or starch in contact with water. The mixture with water, although transparent, yields up the substance on filtration or on heating. The substance separated by heating dries up to a brittle transparent colourless mass, having the composition of methacrylic acid. This decomposes at  $300^\circ$  without yielding a trace of methacrylic acid. The polymeride is a feeble acid; it dissolves in ammonia and is reprecipitated by hydrochloric acid. Barium and calcium chlorides give with the ammoniacal solution white precipitates which coalesce to gummy masses, and become very hard when heated, but resume their elasticity on cooling. When dried at  $100^\circ$ , these precipitates have the composition—



The soluble alkaline salts remain as gums when their solutions are evaporated.

Neither oxidising agents nor fusing potash yield any defined products with the polymeride. Ch. B.

**Decomposition of the Substitution-products of the Lower Fatty Acids by Water.** By G. C. THOMSON (*Annalen*, 200, 75—87).—A solution of *chloracetic acid* is slowly decomposed on boiling, more rapidly as the solution is more dilute. A 10 per cent. solution is about half converted into glycollic acid at the end of 30 hours; a 5 per cent. solution to the extent of 86 per cent. after four days' boiling, completely after eight days' boiling.

This affords the simplest process for preparing glycollic acid. It is only necessary to evaporate the solution several times with water to the state of syrup, and on standing in a desiccator the mass solidifies to pure glycollic acid. Occasionally the acid separates from the syrup in large transparent deliquescent monoclinic prisms. If the syrup be

heated too long, it will on addition of water deposit the anhydride (m. p. 128—130°) described by Fahlberg (*J. pr. Chem.*, N.F., 7, 335); but even then the solution, on filtration and careful evaporation, will yield pure glycollic acid. The anhydride is crystallisable from boiling water, although Fahlberg states that boiling water reconverts it into glycollic acid.

*α-Bromopropionic acid*, prepared by heating propionic acid with bromine at 120—140° and fractional distillation, is completely converted into hydrobromic and ethylidene-lactic acids after 30 hours' boiling with water.

*β-Iodopropionic acid* (4 per cent. solution) is completely decomposed after 16 hours' boiling with water, yielding 9.5 per cent. of acrylic acid and 90.5 per cent. of hydracrylic acid. The former acid may be removed by distillation with water: the latter may be separated from the hydriodic acid by conversion into calcium salt and precipitation by zinc chloride as zinc-calcium double salt (Heintz and Wislicenus).

*α-Bromobutyric acid* (Erlenmeyer, *Ber.*, 10, 636) is converted on prolonged boiling with water into volatile crotonic acid and non-volatile *α*-hydroxyisobutyric acid (Markownikoff, *Annalen*, 153, 244). The former could not be obtained in a crystalline form.

*α-Bromisobutyric acid* (m. p. 45—46°) in 4 per cent. solution is decomposed, after 27 hours' boiling, into hydroxyisobutyric acid and volatile methacrylic acid (= 8 per cent.).

*Theoretical Remarks* (by R. Fittig).—The above brominated acids (see preceding Abstracts) may serve as types of three different classes:—

1st. Those which are decomposed on neutralisation by sodium carbonate at 0° into unsaturated hydrocarbon, sodium bromide, and carbonic anhydride, with traces of unsaturated acid and hydroxy-acid. Such are, bromhydroethylcrotonic, bromhydrotiglic, and bromhydrocinnamic acids, and the addition-compound of Perkin's homologue of cinnamic acid.

2nd. Those which are decomposed by boiling water or alkalis, partly into unsaturated acid and hydrobromic acid, partly into hydroxy-acid. The former decomposition is predominant in the case of bromisobutyric acid, the latter in the case of the substitution-products of the lower fatty acids, bromhydratropic acid, &c.

3rd. Those which cannot exist in presence of water, but are converted by it into hydroxy-acids or into lactones.

As the author has elsewhere pointed out, members of the first class are derived from acids containing the group  $\text{O} : \text{C}(\text{H or C}).\text{COOH}$ , and contain the bromine and carboxyl united to the same carbon atom. The ground for the second of these statements is, that two of these bodies, bromhydrocinnamic and iodhydrocinnamic acids, are undoubtedly analogous to Glaser's phenylactic acid,  $\text{CH}_2\text{Ph}.\text{CH}(\text{OH}).\text{COOH}$ , containing Br in the place of OH. Erlenmeyer, however (*Ber.*, 12, 1607), gives to bromhydrocinnamic acid the constitution



because the corresponding amido-acid is decomposed by hydrochloric acid into ammonia and cinnamic acid, whereas *α*-alanine,



to which it is closely allied, is not so decomposed. The author replies that even  $\beta$ -alanine has not been proved to undergo a similar change; and, moreover, that  $\alpha$ -alanine, although not attacked by hydrochloric acid, evolves ammonia when heated with barium hydrate at  $180^\circ$ . Erlenmeyer also remarks that bromhydroparacoumaric acid is not converted by ammonia into tyrosine,  $\text{CH}_2\text{Ph}.\text{CH}(\text{NH}_2).\text{COOH}$ . Although not attaching any value to this objection, the author states that Posen in his laboratory has never been able to obtain this bromo-acid, paracoumaric acid being invariably converted by hydrobromic acid into an anhydride,  $\text{C}_{18}\text{H}_{14}\text{O}_6$ , analogous to dilactic acid. The chlorostyrenes, to which Erlenmeyer (*loc. cit.*) alludes, have not yet been sufficiently examined.

Only in the case of acrylic and crotonic acids is the constitution of their addition-compounds known. Methacrylic acid is convertible into bromisobutyric acid,  $\text{CH}_2\text{Br}.\text{CHMe}.\text{COOH}$ : and since it corresponds with atropic acid, the addition-compound of the latter is probably  $\text{CH}_2\text{Br}.\text{CHPh}.\text{COOH}$ . This latter is not converted into a hydrocarbon by sodium carbonate, but passes into atrolactic acid. The bromine addition-compound,  $\text{CH}_2\text{Br}.\text{CBrPh}.\text{COOH}$ , gives off carbonic anhydride with the greatest ease.

The fact that acrylic acid combines with hydrobromic acid to form  $\beta$ -bromopropionic acid,  $\text{CH}_2\text{Br}.\text{CH}_2.\text{COOH}$ , would be in Erlenmeyer's favour, were it not that its homologue, solid crotonic acid, yields  $\alpha$ -bromobutyric acid,  $\text{CH}_2\text{Me}.\text{CHBr}.\text{COOH}$  and  $\alpha$ -iodobutyric acid (Hemilian, *Annalen*, 174, 322); and since solid crotonic acid is related to cinnamic acid as atropic is to methacrylic acid, bromhydrocinnamic acid is probably  $\text{CH}_2\text{Ph}.\text{CHBr}.\text{COOH}$ . Erlenmeyer's view would have the undoubted advantage of explaining the formation of unsaturated hydrocarbon from these acids without assuming a transfer of hydrogen from one carbon-atom to another, thus:  $\text{CHPhBr}.\text{CH}_2.\text{COONa} = \text{CHPh}:\text{CH}_2 + \text{CO}_2 + \text{NaBr}$ .

For hydrosorbic acid, the choice of a formula lies between  $\text{CHMe}:\text{CH}.\text{CH}_2.\text{CH}_2.\text{COOH}$  and  $\text{CH}_2\text{Me}.\text{CH}_2.\text{CH}:\text{CH}.\text{COOH}$ , either of which would explain its decomposition into butyric and acetic acids, and its reduction to normal caproic acid. The first is probably correct; for if the second were so, then either its hydrobromo- or dibromo-compound should give off carbonic anhydride when treated with alkalis.

The case of pyroterebic acid is more obscure. Having the constitution  $\text{CHMe}:\text{CH}:\text{CH}.\text{COOH}$  (since it is decomposed by potash into isobutyric and acetic acids, and is reducible to isocaproic acid) its bromhydro-compound might be expected to give off carbonic anhydride in contact with alkalis, whereas it actually forms a lactone. The two reactions are, however, of the same nature: for both primarily depend on the union of the bromine-atom with the hydrogen of the carboxyl-group, the free bond of the oxygen being in one case transferred to the carbon of the carboxyl to form carbonic anhydride, in the other to the carbon of the principal chain to form a lactone.

The peculiarity of constitution which determines the formation of lactones in all probability cannot be expressed by our present constitutional formulæ. In the aromatic series the "ortho" constitution is



commonly supposed to predispose to it. But Perkin (*Chem. Soc. J.*, 1877, 1, 417) has shown that coumarin is the lactone, not of orthocoumaric acid, but of an isomeride as yet unknown, salts of which have been prepared by Williamson, and its stable methyl salt by Perkin. Santonin, again, is the lactone of santonic acid, which may be isolated, but easily decomposes into water and santonin. But this santonic acid by long boiling with barium hydrate passes into santonic acid, which is perfectly stable and corresponds in all respects to orthocoumaric acid. At present this is inexplicable. Ch. B.

**Structure of Sorbic and Hydrosorbic Acids.** By N. MENSCHUTKIN (*Ber.*, 13, 163—165).—The low initial rate of etherification (7.96) of sorbic acid shows that this acid is tertiary, and the high initial rate of etherification of hydrosorbic acid (43.0) indicates the primary nature of the latter acid. The author explains the conversion of tertiary sorbic acid into primary hydrosorbic acid by reduction with sodium-amalgam, by assuming the existence of a bivalent atom of carbon in the former acid. W. C. W.

**$\beta$ -Dipropyl- and  $\beta$ -Diethyl-ethylenelactic Acid; Oxidation of Allyldimethylcarbinol and Diallylcarbinol.** By SCHIROKOFF (*Ber.*, 12, 2375—2376).— $\beta$ -Dipropylethylenelactic acid,  $(\text{CMeH}_2\text{CH}_2)_2\text{C}(\text{OH})\text{CH}_2\text{COOH}$ ,

is obtained by oxidising allyldipropylcarbinol with potassium permanganate. It is a syrup, which is but sparingly soluble in water, and forms a crystalline silver salt.

$\beta$ -Diethylethylenelactic acid,  $\text{CEt}_2(\text{OH})\text{CH}_2\text{COOH}$ , is obtained in a similar manner from allyldiethylcarbinol. It crystallises in needles (m. p.  $72^\circ$ ). The silver salt forms microscopic needles, whilst the potassium salt is not crystalline.

Allyldimethylcarbinol gives hydroxyvalerianic acid on oxidation either with chromic mixture or with potassium permanganate; the yield in the latter case, however, is much better than in the former. Diallylcarbinol on oxidation gives oxalic acid and a non-volatile acid which has not yet been investigated. T. C.

**Stereocaulon Vesuvianum.** By M. COPPOLA (*Gazzetta*, 10, 9—12).—This plant, after being thoroughly cleansed from dust and dried at  $100^\circ$ , gave 11.16 per cent. of ash of the following composition:—

| $\text{SiO}_2$ | $\text{SO}_2$ | $\text{Fe}_2\text{O}_3$ | $\text{Al}_2\text{O}_3$ | $\text{CaO}$ | $\text{MgO}$ | $\text{K}_2\text{O}$ | $\text{Na}_2\text{O}$ |
|----------------|---------------|-------------------------|-------------------------|--------------|--------------|----------------------|-----------------------|
| 46.40          | 1.07          | 20.40                   | 11.13                   | 14.78        | 2.41         | 2.25                 | 0.97                  |

besides traces of phosphoric acid, manganese, &c.

By macerating the plant with milk-of-lime, precipitating the filtrate with basic lead acetate, and decomposing the precipitate with hydrogen sulphide, a reddish-yellow solution was obtained from which ether extracted a white crystalline substance mixed with a brown resin. The crystalline substance after purification melted at about  $180^\circ$ , and on analysis gave numbers closely agreeing with those required by the formula  $\text{C}_4\text{H}_4\text{O}_4$ . It would seem therefore to be succinic acid, but the

author thinks it necessary to more completely investigate the properties of the substance before pronouncing a decided opinion as to its nature.

C. E. G.

**Preparation of Pure Dioxymumaric Acid.** By S. TANATER (*Ber.*, 13, 159).—In order to separate dioxymumaric acid from oxalic and fumaric acids, the mixture of free acids is digested with freshly precipitated nickel oxide and filtered whilst hot. The liquid on cooling deposits crystals of nickel dioxymumarate, which may be purified by recrystallisation.

W. C. W.

**Formation of  $\beta$ -Methoxyglutaric Acid from Diallylmethylcarbinol.** By W. SOROKIN (*Ber.*, 12, 2374).— $\beta$ -Methoxyglutaric acid is obtained by the oxidation of diallylmethylcarbinol with potassium permanganate. It has the consistence of a syrup, decomposes carbonates, and forms salts, of which only those of silver and copper are crystalline. The copper salt,  $(C_6H_7O_5)_2Cu + CuH_2O_2 + H_2O$ , crystallises in small plates. Its mode of formation indicates the following constitution for the acid:  $—COOH.CH_2.CMe(OH).CH_2.COOH$ .

T. C.

**Ethyl-carbamide and some of its Derivatives.** By R. LEUCKART (*J. pr. Chem.* [2], 21, 1—38).—The author has not been able by his numerous experiments to show that the ethyl-carbamides, obtained from ethyl cyanate by the action of ammonia, and from ethylamine cyanate by the re-grouping of its elementary constituents, are isomeric and not identical bodies: but it must be noted that accurate quantitative researches on their relative solubilities, and crystallographic measurements have not been fully carried out.

The nature of the diphenyl-carbamide obtained from both bodies by heating with aniline, and of the diphenyl-biuret prepared by the same reaction from the ether of ethyl-allophanic acid, as well as the constitution of the acetyl-ethyl and benzoyl-ethyl compounds, renders it probable that if urea is to be regarded as the amide of carbamic acid, both ethyl compounds must be considered to be ethylamides of the same acid.

It is possible that the tolerably high temperature which comes into play in the formation of the amide of ethyl-carbamic acid converts it, as well as the ethyl-ammonium cyanate, into the more stable ethyl-amide of carbamic acid. The author had intended to include in his investigations the products which are formed by the action of ammonia on the ether of ethyl-carbamic acid, and of ethylamine on ethyl carbamate, but was unable to do so.

If an ether of ethyl-carbamic acid containing phosphorus could be obtained by the action of ethylphosphine on ethyl chlorocarbonate, and from this by the action of ethylamine a diethyl-phospho-carbamide, and on the other hand if ethyl cyanate would combine with ethylphosphine to form diethyl-phospho-carbamide, the first body would probably be derived from ammonia, whilst the second would have the characteristic properties of a phosphine.

Ethyl-carbamide itself closely resembles ordinary urea in nearly all its reactions; it unites with acids to form salts, and combines with

metallic oxides. Acted on by ethyl chlorocarbonate, it yields an ether of ethylallophanic acid, and under the action of acid chlorides ethyl-carbamides with acid radicles are formed, closely resembling the corresponding compounds of ordinary urea. It resembles urea in its behaviour with oxidising agents and on addition of water, but it differs in this, that condensation products resembling binret cannot be obtained from it: when heated, it passes directly into a mixture of ethers of cyanuric acid. The melting point of ethyl-carbamide and its compounds generally is lower, but their solubility, especially in ether, is greater than that of the compounds of ordinary urea: the specific gravity of urea is also slightly lowered by the substitution of alcohol radicles for hydrogen. G. T. A.

**Synthesis of Cumene.** By A. LIEBMANN (*Ber.*, 13, 45—46).—By the action of an ethereal solution of zinc methide on benzal chloride, the author has obtained cumene,  $C_9H_{12}$ . It boils at  $152.5$ — $153^\circ$ , its sp. gr. at  $17.5^\circ$  is  $0.86576$ . The sulphonic acids prepared from this hydrocarbon and its barium salt agree in their properties with those prepared from cumene, and this would therefore seem to be isopropylbenzene. P. P. B.

**Crystallographic Constants of some Benzene Derivatives.** By G. LA VALLE (*Gazzetta*, 10, 1—6).—Nitro 1 : 2 : 3 tribromobenzene,  $C_6H_3Br_3NO_2$ . The crystals obtained by slow evaporation of the alcohol and ether solution belong to the triclinic system  $a : b : c = 1.00552 : 1 : 0.48230$ . Observed forms 010, 001, 100, 120, 101,  $\bar{1}22$ ; combinations 010, 001, 100, 120, 101,  $\bar{1}22$ ; cleavage parallel to 100; dichroism feeble.

Nitro 1 : 3 diiodobenzene,  $C_6H_3I_2NO_2$ . The sulphur-yellow crystals obtained by slow evaporation of the alcoholic solution, mixed with very little ether belong to the trimetric system  $a : b : c = 0.64734 : 1 : 0.45819$ . Observed forms 010, 011, 110; combinations 010, 011, 100; cleavage parallel to 110.

Mononitrochlorophenol,  $C_6H_4Cl(NO_2).OH$ . Lemon-yellow crystals belonging to the monoclinic system  $a : b : c = 2.8293 : 1 : 1.50923$ .  $\eta = +X : +S = 112^\circ 29'$ . Observed forms 100, 101, 001,  $\bar{1}01$ , 110,  $\bar{1}12$ ; combinations 100, 101,  $\bar{1}01$ , 110,  $\bar{1}12$  and 100, 101,  $\bar{1}01$ , 110; fracture vitreous. The plane of the optic axis is parallel to the plane of symmetry; dichroism feeble.

Dinitriodobenzene,  $C_6H_3I(NO_2)_2$ . Two of these were examined: the first was obtained by the action of nitric acid on  $[I : NO_2 = 1 : 2]$  nitriodobenzene. The sulphur-yellow crystals belong to the triclinic system  $a : b : c = 1.63461 : 1 : 0.939687$ . Observed forms 001, 100, 110, 190, 010,  $\bar{1}10$ , 101, 011,  $\bar{1}01$ , 201; cleavage perfect parallel to 110. The pinacoids 190, 010, are striated parallel to their intersection; dichroism scarcely sensible. The dinitro derivative obtained from 1 : 4 nitriodobenzene by the action of nitric acid, when examined crystallographically gave results almost identical with those just described, and there can be no doubt but that the minute differences observed were due to the presence of a small quantity of some impurity. C. E. G.

**Anethol Derivatives.** By F. LANDOLPH (*Ber.*, 13, 144—148).—

Boronfluoride decomposes boiling anethol, with formation of anisol, and *anethol dihydride*,  $C_{10}H_{14}O$ . (b. p.  $220^{\circ}$ ). *Anethol tetrahydride* or *anethol camphor*,  $C_{10}H_{18}O$ , is obtained together with anisaldehyde by oxidising anethol with nitric acid. This compound boils at  $190-193^{\circ}$ , and yields on oxidation with sulphuric acid and potassium dichromate an acid crystallising in long needles (m. p.  $175^{\circ}$ ), probably anisic acid. The tetrahydride is converted into the *hexhydride*,  $C_{10}H_{18}O$ , by heating with alcoholic potash in sealed tubes; a potassium salt crystallising in needles is also formed at the same time. The hexhydride is a syrupy liquid at the ordinary temperature. It boils at  $198^{\circ}$ , and solidifies at  $0^{\circ}$ , forming needle-shaped crystals, which melt at  $19^{\circ}$ .

Two compounds are produced by the action of alcoholic potash on anethol in sealed tubes, viz.,  $C_{16}H_{16}O_3$  and  $C_{14}H_{16}O_2$ . The former is sparingly soluble in hot water, but dissolves freely in alcohol, ether, and benzene, and is volatile in a current of steam. The crystals melt at  $87^{\circ}$ . The acetate of this diphenol is a yellowish syrupy liquid, which is easily decomposed by heat.

The compound,  $C_{14}H_{16}O_2$ , is a yellow brittle resin (m. p.  $65^{\circ}$ ), not volatile in a current of steam.

The acetate,  $C_{16}H_{18}O_3$ , is a reddish-yellow resin (m. p.  $40^{\circ}$ ).

Two substances are also formed by the action of alcoholic potash on monochloranethol, prepared by treating anethol with phosphorus pentachloride. The chief product is a colourless liquid,  $C_{16}H_{20}O_2$ , of ethereal odour. It is insoluble in water and potash, and boils at  $270^{\circ}$ .

The second product, a liquid soluble in potash, has not been obtained in the pure state.

W. C. W

**Resorcinol Isosuccineïn.** By J. ROSICKI (*Ber.*, 13, 208—209).—This compound is prepared by heating at  $120-150^{\circ}$  a mixture of isosuccinic acid, resorcinol, and sulphuric acid. The unaltered isosuccinic acid and resorcinol are removed from the crude product, by treatment with boiling water; the residue is dissolved in ammonia, and reprecipitated by hydrochloric acid. Resorcinol-isosuccineïn,  $C_{18}H_{14}O_6$ , is a yellowish-brown amorphous substance, soluble in alcohol, in ether, and in alkalis. In the latter case, a liquid having a faint red colour and green fluorescence is formed.

The isosuccinic acid used in these experiments was prepared by boiling  $\alpha$ -bromopropionic acid (Friedel and Machuca, *Annalen*, 120, 286) with 2 parts of potassium cyanide dissolved in 4 parts of water. The cyanopropionic acid obtained in this way is converted into propionic acid by the usual method.

W. C. W.

**Bromine Derivatives from Quinone.** By SARAUW (*Ber.*, 13, 209).—A mixture of mono- and dibromo-quinols is formed by the action of concentrated hydrobromic acid on solid quinone. Under certain conditions an acetic acid solution of quinone yields only the mono-product. Dibromoquinone is prepared by bringing together equal molecules of bromine and quinone, also by the action of 2 molecules of bromine on one of quinol. Tetrabromoquinol is formed when bromanil is heated with hydrobromic acid.

W. C. W.

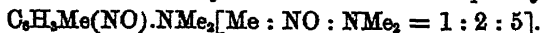
**Action of Sulphur on Phenylbenzamide.** By A. W. HOFMANN (*Ber.*, 12, 2359—2365).—*Benzylumidophenyl mercaptan*,  $C_{13}H_9NS$ , is obtained by boiling 1 part of sulphur with 2 parts of phenylbenzamide for several hours, thus:  $C_{13}H_{11}NO + S = C_{13}H_9NS + H_2O$ . It crystallises from alcohol in colourless needles (m. p.  $115^\circ$ ; b. p. = about that of mercury). It distils without decomposition, and is soluble in ether and in carbon bisulphide. It has feeble basic properties, dissolving in acids to form salts, which are decomposed on addition of water. The platino- and auro-chlorides are described, the latter having the composition,  $2[C_{13}H_9NS.HCl].AuCl_3$ . The free base has an agreeable odour of tea-roses and geraniums, which is considerably increased on warming. Its constitution is represented by the

formula:  $C_6H_5 \begin{array}{c} \diagup N \\ \diagdown S \end{array} CPh$ , the nitrogen being in the ortho-position

as regards the sulphur. This substance is therefore analogous to the compound which Ladenburg obtained (*Ber.*, 9, 1524; 10, 1123) by the action of benzoic chloride on orthamidophenol, for it merely contains sulphur in place of oxygen. On fusion with potash, it gives benzoic acid and *amidophenyl mercaptan*,  $C_6H_4(NH_2).SH$  [1 : 2], the latter of which undergoes oxidation on exposing its solution to the air, crystals of the *bisulphide*,  $(C_6H_4.NH_2)_2S_2$ , being deposited; this reaction takes place more readily if a feeble oxidising agent such as ferric chloride is used; when this latter agent is employed, the *bisulphide-hydrochloride* is first obtained. The hydrochloride crystallises in plates, which are difficultly soluble in very dilute hydrochloric acid, but easily soluble in hot water. By decomposition with ammonia, it gives the bisulphide crystallising in plates (m. p.  $93^\circ$ ), which are insoluble in water, but soluble in boiling alcohol. Reducing agents convert it into the mercaptan. This bisulphide is isomeric with the pseudo-dithioaniline (m. p. =  $79^\circ$ ), obtained by E. B. Schmidt (*ibid.*, 11, 1168) by the action of sulphur chloride on acetanilide.

An impure amidophenylmercaptan has already been obtained by Glutz and Schrank (*J. pr. Chem.*, 2, 223). T. C.

**Constitution of Nitrosodimethylmetatoluidine.** By C. RIEDEL (*Ber.*, 13, 126—127).—Dimethyltolylenediamine obtained by the reduction of nitrosodimethylmetatoluidine, yields on oxidation with sulphuric acid and manganese dioxide, a crystalline compound (m. p.  $67^\circ$ ) which is identical with the toluquinone, which Nietzki (*Ber.*, 10, 838, and this Journal, 1877, ii, 475) prepared from paramidotoluene. This shows that dimethyltolylenediamine is a dimethyl derivative of paramidotoluene, and since this body was obtained by the reduction of nitrosodimethylmetatoluidine, the nitroso-group must occupy the para-position with regard to the amido-group in the latter compound. The constitution of nitrosodimethylmetatoluidine is consequently—



W. C. W.

**Ortho- and Para-toluidine Derivatives.** By G. STAATS (*Ber.*, 13, 135—138).—*Orthotolylthiocarbamide*,  $H_2N.CS.NH.C_6H_3$ , obtained

by the action of ammonia on orthotolylthiocarbimide (b. p. 236°), melts at 155°, and is soluble in hot water and in alcohol. The *para*-compound crystallises in thick needles (m. p. 182°), which are soluble in hot water and alcohol.

*Orthotolylethylthiocarbamide*,  $\text{H} \cdot \text{Et} \cdot \text{N} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , prepared by treating tolylthiocarbimide with ethylamine, crystallises in pale yellow prisms (m. p. 84°), which dissolve in alcohol and ether, but are insoluble in water. The *para*-compound forms crystalline plates (m. p. 93°) soluble in ether and in boiling water.

*Orthotolylphenylthiocarbamide*,  $\text{H} \cdot \text{Ph} \cdot \text{N} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$  (m. p. 139°), crystallises in yellow needles freely soluble in alcohol and ether. *Para*-tolylphenylthiocarbamide (m. p. 137°) is sparingly soluble in water and easily soluble in alcohol and ether.

*Orthotolylglycocine*,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$ , is produced when orthotoluidine monochloracetate is boiled with water for 15 minutes, and is deposited from the mixture on cooling in white acicular crystals (m. p. 150°). Orthotolylglycocine forms a crystalline compound with copper salts; it reduces nitrate of silver solution, and throws down a red precipitate when boiled with ferric chloride.

*Acetorthohomoparaoxybenzaldehyde*,  $\text{C}_6\text{H}_4 \cdot \text{Me}(\text{OAc}) \cdot \text{COH}$ , is obtained in needle-shaped crystals (m. p. 40°) by adding an ethereal solution of acetic anhydride to the potassium salt of orthohomoparaoxybenzaldehyde.

W. C. W.

**A New Base.** By E. F. SMITH (*Ber.*, 13, 33—34).—By the perchlorination of toluene, the author has obtained a carbon chloride,  $\text{C}_{21}\text{Cl}_{36}$ , which crystallises in large colourless prisms, m. p. 152—153° (*Am. Phil. Soc.*, May 4, 1877; *Jahresb.*, 1877, p. 420). By the action of this chloride on aniline in sealed tubes at 180°, the new base is obtained. It is easily soluble in water and other solvents, and has been obtained from concentrated aqueous solutions in thin leaflets, which blacken at 225° and melt at 230°. When warmed with aqueous solution of chromic acid, it is converted into a reddish-brown mass, only sparingly soluble in water, but soluble in alcohol with an intense red coloration. The new base forms well crystallised salts; the hydrochloride forms long thick needles, easily soluble in alcohol and water.

P. P. B.

**A Series of Aromatic Bases Isomeric with the Thiocarbimides.** By A. W. HOFMANN (*Ber.*, 13, 8—22).—The author has already described (this Journal, 1879, Abstr., 805) the production of chlorophenylthiocarbimide,  $\text{C}_6\text{H}_4\text{ClNS}$ . It is a liquid which crystallises on cooling (m. p. 24°). It has basic properties; its solution in concentrated hydrochloric acid is precipitated by gold and platinum chlorides, the double salt so formed being decomposed by water, forming chlorophenylthiocarbimide.

Chlorophenylthiocarbimide is decomposed by water at 200°, aniline, hydrochloric acid, carbonic anhydride, and sulphur being amongst the products of the reaction.

*Chloronitrophenylthiocarbimide*,  $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)\text{NS}$ , is obtained by the action of nitric acid on the solution of the thiocarbimide in concen-

trated sulphuric acid. It crystallises in yellow needles, m. p.  $192^{\circ}$ , and is destitute of basic properties. The chlorine in this compound may be replaced, e.g., by aniline, forming a compound melting at  $247^{\circ}$ .

*Ethoxyphenylthiocarbimide* is obtained by treating the chlorophenylthiocarbimide with solution of sodium ethylate in alcohol. It forms at first an oil, which finally becomes crystalline, m. p.  $25^{\circ}$ . It has feeble basic properties, being dissolved by hydrochloric acid, and yields unstable auro- and platino-chlorides.

*Acetoxyphenylthiocarbimide*,  $C_7H_4(OAc)NS$ , is obtained by heating hydroxyphenylthiocarbimide (*loc. cit.*) with acetic anhydride. It crystallises from alcohol in prisms, and from hot acetic acid in needles, melting at  $60^{\circ}$ . It has no basic properties.

*Amyldophenylthiocarbimide* (*loc. cit.*) is precipitated from its alcoholic solutions in shining leaflets melting at  $129^{\circ}$ . It may be distilled without decomposition. It is a feeble base, dissolving in concentrated acids. Platinum and gold chlorides precipitate its hydrochloric acid solutions; the double salts so obtained are not decomposed by water. The platinochloride has the composition  $[C_7H_4(NH_2)NS.HCl]_2PtCl_4$ .

*Aulidophenylthiocarbimide* (*loc. cit.*) after repeated crystallisation melts at  $159^{\circ}$ , not  $157^{\circ}$  as formerly stated. It is very stable, may be distilled, and is not decomposed by boiling with alkalis or acids. Its platinochloride has the composition  $[C_7H_4(NHPh)NS.HCl]_2PtCl_4$ .

The 1.2, 1.3, and 1.4 chloranilines were converted into carbamides by means of carbon bisulphide, and the corresponding chlorophenylthiocarbimides obtained from them.

1.2 chloraniline yields a thiocarbamide (m. p.  $145-146^{\circ}$ ), and a solid thiocarbimide (m. p.  $44-45^{\circ}$ , b. p.  $249-250^{\circ}$ ).

1.3 chloraniline yields a thiocarbamide (m. p.  $121-122^{\circ}$ ), and a liquid thiocarbimide (b. p.  $249-250^{\circ}$ ).

1.4 chloraniline yields a thiocarbamide (m. p.  $168^{\circ}$ ), and a solid thiocarbimide (m. p.  $44.5^{\circ}$ , b. p.  $249-250^{\circ}$ ).

None of these chlorophenylthiocarbimides exhibit the same properties as that prepared from phenylthiocarbimide (*loc. cit.*). The chlorine in this compound may be replaced by hydrogen, e.g., when it is treated with tin and hydrochloric acid or hydriodic acid and phosphorus, and thus a new base is obtained isomeric with phenylthiocarbimide and phenylthiocyanate.

This base,  $C_7H_5NS$ , is a liquid heavier than water, in which it is scarcely soluble; alcohol and carbon bisulphide dissolve it easily. It has a burning taste, and an odour resembling that of the pyridine bases. It boils at  $230^{\circ}$ . It forms salts, and its hydrochloride yields a crystalline, sparingly soluble platinochloride,  $[C_7H_5NS.HCl]_2PtCl_4$ , and an aurochloride,  $C_7H_5NS.HCl.AuCl_3$ , also double salts with tin and mercuric chlorides. Moreover, this base differs from phenylthiocarbimide, inasmuch as the sulphur is not removed by alkalis or by lead. It forms addition-products with bromine and with methyl iodide; the latter crystallises in needles melting at  $210^{\circ}$ , and having the formula  $C_7H_5NS.MeI$ . The base, treated with phosphorus pentachloride, yields the original chlorophenylthiocarbimide.

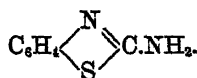
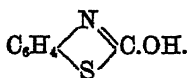
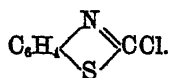
*Phenyl-phenylthiocarbimide*,  $C_7H_4(C_6H_5)NS$ .—This body is obtained in small quantities when phenylthiocarbimide is heated with benzoic chloride at  $250-300^\circ$ , thus:  $C_7H_5NS + PhCOCl = C_7H_4PhNS + CH_3OCl$ . It crystallises from alcohol in beautiful needles having the odour of roses and geraniums. This body is identical with that obtained by the action of sulphur on phenylbenzamide (this vol., p. 386).

The new base,  $C_7H_5NS$ , when fused with alkalis is resolved into formic acid and amidophenyl mercaptan, and further it may be prepared by heating these two compounds together. Therefore it is

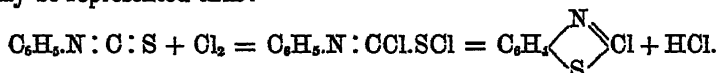
*methenylamidophenyl mercaptan*,  $C_6H_4 \begin{array}{c} \diagup N \\ \diagdown S \end{array} CH$ .

The author has prepared the amido-mercaptans from the 1. 2, 1. 3, and 1. 4 nitrobenzenesulphonic acids described by Limpricht (*Annalen*, 177, 60).

1. 2  $C_6H_4(NO_2).SO_3H$  gave an amide,  $C_6H_4(NO_2).SO_2NH_2$ , m. p.  $188^\circ$ , which on reduction gave an amido-mercaptan. Similarly 1. 3- $C_6H_4(NO_2).SO_3H$  yielded an amide, m. p.  $164^\circ$ , and finally 1. 4- $C_6H_4(NO_2).SO_3H$  gave an amide, m. p.  $131^\circ$ , from both of which amides mercaptans were obtained by reduction. The mercaptans from 1. 3 and 1. 4 nitrosulphonic acids are not acted on by acids or by acid chlorides, whereas the 1. 2 mercaptan when heated with formic acid yields the base  $C_7H_5NS$ . Thus the constitution of this base being represented by the above formula, those of the chloro-, hydroxy-, and amido-derivatives are as follows:—



And the formation of the chloro-derivative from the thiocarbimide may be represented thus:—



The following homologues of methenylamidophenyl mercaptan have been prepared:—

*Ethenylamidophenyl mercaptan*,  $C_6H_7NS$ , is obtained by the action of acetic anhydride on the amidomercaptan. It resembles the methenyl compound in its properties, and boils at  $238^\circ$ . The platinochloride,  $(C_6H_7NS.HCl).PtCl_4$ , forms yellow needles.

*Propenylamidophenyl mercaptan*,  $C_9H_9NS$ , obtained from the amidomercaptan and propionic chloride. It is a colourless heavy liquid, boiling at  $252^\circ$ . Its platinochloride forms large prisms.

*Pentenylamidophenyl mercaptan*,  $C_{11}H_{13}NS$ , is obtained from the amidomercaptan and valeric chloride. It has less marked basic properties than the lower homologues; its platinochloride is obtained as a crystalline precipitate by treating the alcohol solution with hydrochloric acid and platinum chloride.

P. P. B.

**Some Azo-derivatives.** By F. STEBBINS (*Ber.*, 13, 43—44).—*Azobenzenetrinitro-xybenzene*,  $C_6H_5.N_2.C_6H(NO_2)_3.OH$ , is obtained by



treating an alcoholic solution of picric acid with diazobenzene nitrate. It is an unstable compound, crystallises in long brown prismatic needles, having metallic lustre; when heated to  $70^{\circ}$  it explodes. It is insoluble in cold water, slightly soluble in hot water, and easily in alcohol. It dyes silk and wool orange-yellow.

*Azobenzenepyrogallol*,  $C_6H_5.N_2.C_6H_2(OH)_3$ , is obtained by treating an alkaline solution of pyrogallol with diazobenzene nitrate. When crystallised from glacial acetic acid, it forms small red needles, insoluble in water, but easily soluble in alcohol and in nitrobenzene. It also dyes silk and wool orange-yellow. P. P. B.

**Dye-stuffs of the Rosaniline Group.** By E. and O. FISCHER (*Ber.*, 12, 2344—2353).—In a previous communication (*ibid.*, 800), the authors described a green dye-stuff obtained from paranitrobenzoic chloride and dimethylaniline; this they considered to be the paranitro-derivative of malachite green. By reduction with zinc-dust and acetic acid, this body gives a violet dye-stuff very similar to the violet derivatives of rosaniline. On further reduction, a leuco-base is obtained, which appears to be a methylated leuco-aniline. This on oxidation yields a violet-red dye, and by heating with methyl iodide gives an ammonium base as a final product identical with the compound obtained from paraleucaniline in a similar way. The final methylated product of ordinary leucaniline is a nono-, and not an octo-methylated compound, as stated by Hofmann and Girard (*ibid.*, 2, 448).

*Nonomethylated paraleucaniline*,  $C_{12}H_{13}Me_9(MeI)_3$ , crystallises from hot water in colourless needles and possesses properties similar to those of its homologue. On heating the iodide, it loses methyl iodide, and is partially converted into methyl violet. These properties are also exhibited by the body obtained from the leuco-base of paranitro-bitter almond oil green by heating with methyl iodide and methyl alcohol at  $100$ — $110^{\circ}$ .

The ammonium iodides of both compounds when heated quickly in capillary tubes assume a feeble blue colour, and melt with evolution of gas at  $185^{\circ}$  to a dark violet-blue liquid. They are therefore identical, and the relative position of the three nitrogen groups in the green nitro-compound is the same as in pararosaniline, and further, it is very probable that the two amido-groups have the same position as in malachite green, there being in fact no essential difference between the constitution of the two bodies. Their direct conversion by reduction into a violet methylated rosaniline derivative shows that the whole class of dye-stuffs derived from bitter almond oil green has a constitution similar to that of rosaniline.

From considerations for which the original paper must be consulted, it appears that the colour-forming group in all the basic derivatives of triphenyl carbinol is essentially the same.

In regard to the cause of the difference in colour of methyl-violet and methyl-green, the following conclusions are drawn:—Since the colour of the paranitro-benzaldehyde green is not essentially different from that of benzaldehyde oil green, it would seem that the colour is independent of the nitro-group; but when the latter becomes an

amido-group, the green changes to reddish-violet. The two methylated amido-groups in benzaldehyde green are therefore the cause of the green colour, and these, when in combination with a third amido-group present in the para-position, give a red. When, however, this third amido-group is destroyed, the green colour is reproduced, as is the case when the third amido-group is changed into a quarternary ammonium-group, which, like the nitro-group, is without influence on the colour, but increases the solubility of the dye-stuff.

Hofmann's (*ibid.*, 7, 364) tri-iodomethylated trimethylrosaniline is totally different from methyl-green. T. C.

**Safranine.** By R. BINDSCHIEDLER (*Ber.*, 13, 207—208).—*Safranine* is best prepared by the action of potassium chromate on a dilute boiling solution of paradiamidotoluene hydrochloride (1 mol.) and ortho- or para-toluidine hydrochloride (2 mols.). On neutralising the liquid with sodium carbonate, the safranine remains in solution. A similar colouring matter is produced by oxidising a mixture of dimethylphenyldiamine (1 mol.) and aniline hydrochloride (2 mols.). The alcoholic solution which is strongly fluorescent dyes silk bright red.

By oxidising a cold dilute hydrochloric acid solution of dimethylphenylenediamine (1 mol.) and dimethylaniline (2 mols.) in presence of zinc chloride, beautiful crystals are produced, having a cuprous or green lustre. The aqueous solution has an intense green colour; when heated with aniline hydrochloride, it yields a reddish-violet fluorescent liquid. W. C. W.

**Colouring Matters from Furfuraldehyde.** By H. SCHIFF (*Annalen*, 201, 355—369).—Furfuraldehyde combines with 2 molecules of diphenylamine at 150° to form an oily liquid, which solidifies at 0° to a crystalline mass. With hydrochloric acid this substance yields a bronze-coloured compound, which dissolves in alcohol, forming a deep-red coloured solution. The hydrochloride is unstable, and cannot be purified by recrystallisation.

When an alcoholic solution of metanitrilaniline and furfuraldehyde is gently warmed, the compound  $C_6H_4(NO_2).NH_2.C_5H_4O_2$  separates out as a chrome-yellow crystalline crust. The hydrochloride of this base crystallises in small plates, having a metallic lustre. The deep carmine colour of the alcoholic solution is destroyed by strong hydrochloric acid.

*Hydroxyfurfuraniline* is deposited in pale yellow prisms, when aqueous solutions of furfuraldehyde and paramidophenol are mixed together,  $C_6H_4(OH).NH_2 + C_5H_4O_2 = H_2O + C_6H_4 : (OH).N.C_5H_4O$ .

The crystals are soluble in alcohol; they melt at 180°, undergoing decomposition. The hydrochloride could not be obtained by direct union of the base with hydrochloride acid, but it may be easily prepared by evaporating at 60°, an alcoholic solution of the base containing a small quantity of ammonium chloride. It forms a beetle-green crystalline mass, sparingly soluble in water, but dissolving freely in alcohol, producing a red solution.

*Difurfurolitylenediamine*,  $C_{17}H_{18}N_2(C_5H_4O)_2$ , prepared by adding furfuraldehyde to an alcoholic solution of metatolylenediamine, crys-

tallises in orange-coloured needles, which decompose at  $120^{\circ}$  without melting. The carmine-coloured hydrochloride is soluble in alcohol and in water, but is decomposed by a large excess of the latter solvent. The platinumchloride has the composition,  $H_2PtCl_6 \cdot C_7H_{10}N_2 \cdot 2C_6H_4O_2$ . The preparation of *furfurobenzidine*  $(C_6H_4N)_2(C_6H_4O)_2$  resembles that of the preceding base. It forms pale yellow needles, which are only sparingly soluble in water and in cold alcohol, but dissolve freely in benzene. The salts of furfurobenzidine are very unstable; they form carmine-coloured alcoholic solutions. The hydrochloride has the composition  $C_{12}H_{12}N_2 \cdot 2C_6H_4O_2 \cdot 2HCl$ .

*Furfuramidobenzoic acid*,  $C_6H_4(NH_2)COOH \cdot C_5H_4O_2$ , is deposited in dichroic needle-shaped crystals, when furfuraldehyde is added to an aqueous solution of amidobenzoic acid. The compound is soluble in alcohol, forming a red solution. It has neither acid nor basic properties. If in the preceding reaction a salt of amidobenzoic acid is used instead of the free acid, no coloured derivative is obtained until hydrochloric acid is added to the mixture.

Amidocinnamic and the amidosalicylic acids also yield crystalline compounds with furfuraldehyde. W. C. W.

**Nitration of Metachlorosalicylic Acid.** By E. F. SMITH and G. K. PERCE (*Ber.*, 13, 34—36).—By the nitration of metachlorosalicylic acid, metachloronitrosalicylic acid and two isomeric *dinitrochlorophenols* were obtained. The two phenols were separated by means of their potassium salts, the less soluble one proving to be the  $\alpha$ -monochlorodinitrophenol described by Faust and Saame. The isomeride of this phenol crystallises in orange needles (m. p.  $78-80^{\circ}$ , and solidifying at  $25^{\circ}$ ). Its potassium salt crystallises in orange-coloured needles, containing  $1\frac{1}{2}$  mol. of water, and is easily soluble in water. The silver salt of the  $\alpha$ -derivative forms long red needles, whilst that of the isomeride forms bronze, lustrous needles.

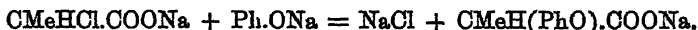
The *nitrochlorosalicylic acid* crystallises in needles (m. p.  $162-163^{\circ}$ ), and is identical with metachloronitrosalicylic acid described by Hubner. The *potassium* salt,  $C_6H_2Cl(NO_2)(OH).COOK$ , forms yellow needles, having a bitter taste; is easily soluble in water. The *barium* salt  $[C_6H_2Cl(NO_2)(OH).COO]_2Ba$  forms orange-red needles sparingly soluble in water. The *ethyl* salt,  $C_6H_2Cl(NO_2)(OH).COOEt$ , crystallises in colourless needles, melting at  $89^{\circ}$ ; from it the amide,  $C_6H_2Cl(NO_2)(OH).CONH_2$ , has been obtained; it is easily soluble in alcohol, but sparingly in water (m. p.  $199^{\circ}$ ).

$\alpha$ -*Monochlorodinitrophenolaniline*,  $C_6H_2Cl(NO_2)_2.OH \cdot C_6H_5.NH_2$ , is obtained by mixing the phenol with aniline, when a deep-red solution is formed. By evaporation, it is obtained in hard yellow crystals which are easily soluble in hot water, and melt at  $137^{\circ}$ . It is resolved into its constituents by continued boiling with water. P. P. B.

**Action of Phenols on Halogen-derivatives of Fatty Acids.** By L. SAARBACH (*J. pr. Chem.* [2], 21, 151—171).—The reaction of phenol with monochloroacetic acid, yielding phenoxyacetic acid, was regarded by Heintz, who first studied it (*Pogg. Ann.*, 109, 489), as typical of

the whole series of possible homologous reactions. The investigation of certain of these forms the subject of this communication.

*Phenol and  $\alpha$ -Monochloropropionic Acid.*—These bodies, in the form of their sodium compounds, react in the cold with formation of phenoxypropionic acid (m. p. 112.5°), thus:—

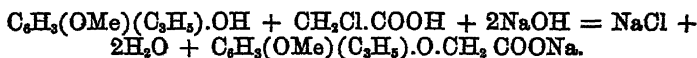


This acid is freely soluble in alcohol, ether, and in hot water; slightly soluble in cold water. It is volatilised by steam. The aqueous solution gives a yellowish precipitate with ferric chloride. The *sodium* salt, the product of the above reaction, crystallises on evaporation of its aqueous solution in concentric groups of needles; the *potassium* salt also in long needles containing  $1\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ . *Ethyl phenoxypropionate*,  $\text{CMeH(OPh).COOEt}$ , is easily prepared by passing hydrochloric acid gas into the alcoholic solution of the acid kept boiling on the water-bath. It is a colourless liquid of sp. gr. 1.360 at 17.5°; it boils undecomposed at 243–244°; it is volatilised by steam. In contact with aqueous ammonia it is decomposed, yielding the corresponding amide:



It is freely soluble in alcohol, ether, and hot water, crystallising from its solutions in needles (m. p. 130°). On adding bromine to the hot aqueous solution of phenoxypropionic acid, *monobromphenoxypropionic acid*,  $\text{CMeH(OC}_6\text{H}_4\text{Br).COOH}$ , is formed. On recrystallising from dilute alcohol, it is obtained in long transparent needles (m. p. 105–106°), which are freely soluble in ether and alcohol: on the addition of water to its solution in the latter, the acid is separated. The acid is not decomposed by boiling with concentrated solution of soda.

*Eugenol and Monochloroacetic Acid.*—These bodies were heated together on the water-bath, and soda (sol. sp. gr. 1.34°) added, until the decomposition was complete. The reaction which occurs is expressed by the equation:—



The new acid crystallises from its aqueous solution in long needles (m. p. 80–81°), which are easily soluble in ether and in alcohol.

*Thymol and Monochloroacetic Acid.*—The reaction which occurs is exactly analogous to the preceding. The thymoxyacetic acid formed,  $\text{C}_6\text{H}_3\text{Me(PrO).CH}_2\text{COONa}$ , is freely soluble in alcohol, ether, and hot water, and crystallises from its solution in long needles (m. p. 148°).

*Orcinol and Monochloroacetic Acid.*—The reaction between these bodies, which is equally smooth, takes place according to the equation:—



The acid is easily isolated, crystallising from its hot aqueous solution in microscopic needles (m. p. 216–217°). Its analogy with the acid previously described suggests the name diorcoxydiacetic acid;

the term diocroxy- representing the hypothetical diatomic radicle,  
 $\left( \text{C}_6\text{H}_5\text{Me} \begin{Bmatrix} \text{O} \\ \text{O} \end{Bmatrix} \right)$ .

The normal sodium salt crystallises from its aqueous solution with 8 mols.  $\text{H}_2\text{O}$ . The calcium salt crystallises with 2 mols.  $\text{H}_2\text{O}$  in thin plates. *Ethyl diocroxydiacetate* is prepared by passing hydrochloric acid gas into the hot alcoholic solution of the acid. It is freely soluble in alcohol and ether, crystallising from these solutions in needles (m. p.  $107^\circ$ ); on the addition of water, it separates as an oil. In contact with aqueous ammonia, it is converted into the corresponding amide.

Two isomeric mononitrodioroxydiacetic acids are formed when the acid is added slowly to warm concentrated nitric acid; one of these is separated as a red powder on diluting the solution; the second is obtained in the form of colourless monoclinic prisms by evaporating the filtrate from the first, allowing to crystallise, and recrystallising from alcoholic solution.

*Phenol and Dibromosuccinic Acid*.—The mutual reaction of these bodies was investigated; but the results obtained were not of a definite character.

C. F. C.

**Condensation-products of Gallic Acid.** By J. OSER and F. BÖCKER (*Wien. Akad. Ber.*, 79 [2], 148—155).—By mixing gradually and with certain precautions a solution of potassium permanganate with one of gallic acid containing sulphuric acid, the authors obtained a yellow substance, which in a pure state formed minute acicular crystals. Its composition agreed with the formula  $\text{C}_{14}\text{H}_{10}\text{O}_8$ , and when heated with zinc powder in hydrogen, it yielded a hydrocarbon corresponding with the formula  $\text{C}_{14}\text{H}_{10}$ , and identical with that which Rembold obtained by a similar reduction of ellagic acid (*Ber.*, 1875, 1494), and proposed to designate by the name of *ellagene*. The authors consider, therefore, that their new substance is not to be ranked in the series of condensation-products of rufigallic acid, but belongs to the ellagic acid series, its relation to ellagic acid,  $\text{C}_{14}\text{H}_6\text{O}_8$ , being that of a reduction-product to an oxidation-product.

R. R.

**Sulphonic Acids from Isomeric Nitramido- and Diamido-benzenes.** By J. POST and E. HARDTUNG (*Ber.*, 13, 38—41).—*Orthonitramidobenzene-sulphonic acid*, prepared from orthonitraniline by the action of fuming sulphuric acid, is easily soluble in alcohol and water. The barium salt,  $[\text{C}_6\text{H}_3(\text{NO}_2).\text{NH}_2\text{SO}_3]_2\text{Ba}.2\frac{1}{2}\text{H}_2\text{O}$ , forms dark yellow brittle needles. The calcium salt,  $[\text{C}_6\text{H}_3(\text{NO}_2).\text{NH}_2\text{SO}_3]_2\text{Ca}.2\frac{1}{2}\text{H}_2\text{O}$ , is soluble in 4—6 times its weight of boiling water; it crystallises in bright yellow needles. The potassium salt crystallises with 1 mol. of water in dark yellow short needles which are more soluble than the above.

*Orthodiamidobenzene-sulphonic acid* is obtained by the reduction of the nitramido-acid; it forms rose-coloured needles. Its barium salt,  $[\text{C}_6\text{H}_3(\text{NH}_2).\text{NH}_2\text{SO}_3]_2\text{Ba}.5\frac{1}{2}\text{H}_2\text{O}$ , is very soluble in water; crystallises in thin, light brown leaflets. It is precipitated from its aqueous solutions by alcohol in the form of brittle, bright brown needles. The calcium salt,  $[\text{C}_6\text{H}_3(\text{NH}_2).\text{NH}_2\text{SO}_3]_2\text{Ca}.3\text{H}_2\text{O}$ , is also easily soluble in

water. The orthodiamidobenzene-sulphonic acid, prepared from orthodiamidobenzene, is identical with the above, showing that the sulphonyl-group replaces the same atom of hydrogen in the aromatic nucleus, whether there be a nitro- and an amido-group present, or two amido-groups.

*Metanitramidobenzene-sulphonic acid* is prepared by heating metanitraniline with fuming sulphuric acid in sealed tubes at  $175^{\circ}$ . The free acid prepared from its barium salt crystallises in large yellow brown prisms. The *barium* salt,  $[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NH}_2\text{SO}_3]_2\cdot\text{Ba}\cdot 2\text{H}_2\text{O}$ , is soluble in 6—8 times its weight of hot water, crystallises in dark brown needles. By slow evaporation of its aqueous solutions, it is obtained in tables. The *calcium* salt,  $[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NH}_2\text{SO}_3]_2\cdot\text{Ca}\cdot 4\text{H}_2\text{O}$ , is easily soluble in hot water, from which it crystallises in small, dark yellow needles.

*Metadiamidobenzene-sulphonic acid*, prepared by the reduction of the metanitroamido acid, has been obtained in two dimorphous modifications. Its *barium* salt,  $[\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{NH}_2\text{SO}_3]_2\cdot\text{Ba}\cdot 6\text{H}_2\text{O}$ , is easily soluble in water, less soluble in alcohol and water; it crystallises in brown prisms. The *calcium* salt,  $[\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{NH}_2\text{SO}_3]_2\cdot\text{Ca}\cdot 5\frac{1}{2}\text{H}_2\text{O}$ , crystallises from a mixture of alcohol and water in colourless, compact prisms, which are very soluble in water.

The metadiamidobenzene-sulphonic acid, prepared from metadiamidobenzene, is identical with that obtained from metanitramidobenzene sulphonic acid, as was the case with the orthodiamidobenzene sulphonic acids.

P. P. B.

**Synthesis of Methylketole, an Isomeride of Skatole.** By A. BÄYER and O. R. JACKSON (*Ber.*, 13, 187—189).—*Methylketole*,

$\text{C}_6\text{H}_5\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C.Me}$ , is formed by treating the nitro-derivative of the

methylketone of phenylacetic acid (*Ber.*, 3, 198) with ammonia and zinc-dust, at a temperature just below the boiling point of the mixture. When the product is distilled in a current of steam, the methylketole crystallises from the distillate in colourless plates or needles, which have a strong odour, resembling that of indole.

The crystals melt at  $59^{\circ}$ , and distil without decomposition at a higher temperature. They are soluble in hot water and in cold hydrochloric acid. The acid solution yields a crystalline platinumchloride, and a deposit of yellowish-red needles with picric acid. With nitrous acid a yellowish, and with bleaching powder a fugitive blue, coloration is produced.

W. C. W.

**Monophenylboron Chloride. The Quantivalence of Boron.** By A. MICHAELIS and P. BECKER (*Ber.*, 13, 58—61).—*Monophenylboron chloride* is prepared by the action of mercury diphenyl on boron chloride at  $180$ — $200^{\circ}$ , the following reaction taking place,  $\text{Hg}(\text{C}_6\text{H}_5)_2 + 2\text{BCl}_3 = 2\text{C}_6\text{H}_5\text{BCl}_2 + \text{HgCl}_2$ . It is a colourless liquid, becoming red on exposure to the air; it boils at  $175^{\circ}$ : like boron chloride, it fumes in the air, and decomposes with a hissing noise when treated with water.

By this action *monophenylboric acid* is produced, which crystallises from water in needles. Chlorine is not absorbed by monophenylboron chloride at the ordinary temperature, but a small quantity of the chloride is decomposed as follows:  $C_6H_5BCl_2 + Cl_2 = C_6H_5Cl + BCl_3$ . If monophenylboron chloride be placed in a freezing mixture, it solidifies, and in this state absorbs chlorine, becoming at the same time liquid, owing to the formation of a tetrachloride,  $C_6H_5BCl_4$ , which when removed from the freezing mixture decomposes, forming boron chloride and chlorobenzene, thus:  $C_6H_5BCl_4 = C_6H_5Cl + BCl_3$ . At the same time a portion decomposes into the monophenylboron chloride and chlorine, thus:  $C_6H_5BCl_4 = C_6H_5BCl_2 + Cl_2$ .

The formation of this tetrachloride and its decomposition, the authors regard as evidence of the quinquivalence of boron.

P. P. B.

**Aromatic Arsenic Compounds.** By W. LA COSTE and A. MICHAELIS (*Annalen*, 201, 189—261).—After referring to the researches of Bunsen (*Annalen*, 24, 271; 31, 175; 37, 1; 42, 25; 46, 1), Dumas (*ibid.*, 27, 148), Cahours and Riche (*Compt. rend.*, 36, 1001; 39, 541; 49, 87, and 50, 1002), Landolt (*Annalen*, 89, 301; 92, 365), Wohler (*ibid.*, 103, 375), Hofmann (*ibid.*, 103, 357, and Supplement, 1, 306), and Baeyer (*ibid.*, 105, 265), on the organic arsenic compounds, the authors give an account of the mono-, di-, and tri-phenyl- and of the mono-tolylarsinic derivatives. Most of these bodies have been previously described (*Ber.*, 8, 1316; 9, 1566; 10, 622; 11, 1883, and this Journal, 1876 [i], 610; 1877 [i], 311; [ii], 452; 1879, Abstracts, 161).

*Monophenylarsinic acid*,  $PhAsO(OH)_2$ , is soluble in aqueous ammonia, potash, soda, and baryta-water.

When a concentrated solution of the ammonium salt is allowed to stand over sulphuric acid, it slowly deposits transparent needle-shaped and prismatic crystals, which lose ammonia and effloresce on exposure to the air. The *potassium* salt,  $PhAsO(OH).OK$  is very hygroscopic, and has not been obtained in the crystalline state. The *barium* salt  $(PhAsO_2H)_2Ba$  forms anhydrous needle-shaped crystals, which are less soluble in hot than in cold water. Monophenylarsinic acid forms two *calcium* salts; the acid salt,  $(PhAsO_2H)_2Ca$ , prepared by adding ammonia to a boiling concentrated solution of calcium chloride and phenylarsinic acid, until the mixture is but slightly acid, is sparingly soluble in hot water. By recrystallisation from hot dilute hydrochloric acid, the salt is obtained in colourless needles. The neutral calcium salt,  $PhAsO_2Ca + 2H_2O$ , is deposited in clusters of needle-shaped crystals, when a layer of ammonia is cautiously poured on a dilute mixture of calcium chloride and phenylarsinic acid. The copper and lead salts are insoluble in water.

*Diphenylarsenious chloride*,  $Ph_2AsCl$ , is prepared by the action of mercury-diphenyl on an excess of monophenylarsenious chloride; the best yield is obtained when the temperature of the mixture is rapidly raised above  $320^\circ$ . The pure chloride is a pale yellow oil (b. p.  $333^\circ$ , sp. gr. 1.42231 at  $15^\circ$ ) insoluble in water, but soluble in alcohol, ether, and benzene. It combines directly with chlorine and bromine to form solid addition products. It is attacked by zinc at  $100^\circ$  with the pro-

duction of a small quantity of a crystalline compound (m. p.  $154^{\circ}$ ), which dissolves freely in benzene.

*Diphenylarsinic acid*,  $\text{Ph}_2\text{AsO}_2\text{H}$ , is deposited from an aqueous solution in needles and from an alcoholic solution in prisms (m. p.  $174^{\circ}$ ). The acid resists the action of oxidising agents.

The *ammonium* salt separates from a concentrated solution in feathery crystals which rapidly lose ammonia at the ordinary temperature. The *sodium* salt,  $\text{Ph}_2\text{AsO}_2\text{Na}$  is very hygroscopic.

The *barium* salt  $(\text{Ph}_2\text{AsO}_2)_2\text{Ba}$  forms a gum-like mass soluble in water and alcohol, the *calcium* salt is deposited in woolly needles on the addition of ether to its solution in alcohol.

The *lead* salt is sparingly soluble in boiling water; anhydrous silky crystals are deposited from the solution on cooling. The *copper* salt is insoluble in water.

*Triphenylarsine*,  $\text{AsPh}_3$ , is most easily prepared by the decomposition of the monophenylarsenious oxide,  $3\text{PhAsO} = \text{AsPh}_3 + \text{As}_2\text{O}_3$ . The mixture of mono- and di-phenylarsenious chlorides obtained by the action of arsenious chloride on benzene is converted into oxide by boiling with sodium carbonate. The oxide is heated at  $180^{\circ}$  for some time and then slowly distilled until the temperature reaches  $360^{\circ}$ ; the residue in the retort is dissolved in alcohol and treated with animal charcoal. On evaporating the solution, triphenylarsine crystallises in transparent colourless plates (m. p.  $58^{\circ}$ ). The crystals are insoluble in water and in hydrochloric acid, but dissolve freely in benzene and ether. Triphenylarsine is not attacked by ethyl iodide, but it combines directly with sulphur to form  $\text{Ph}_3\text{AsS}$ . The sulphide is best prepared by boiling triphenylarsenious dichloride with yellow ammonium sulphide; the mixture is acidified with hydrochloric acid, and on recrystallising the precipitate from alcohol the sulphide is obtained in silky needles (m. p.  $162^{\circ}$ ).

The *monotolylarsenous oxides*,  $\text{C}_6\text{H}_4\text{Me.AsO}$ , are prepared by boiling the ortho- and para-tolylarsenious chlorides with a concentrated solution of sodium carbonate. The resinous product is extracted with hot water and dissolved in alcohol; on evaporating the alcoholic solution to dryness and washing the residue with cold ether, the tolylarsenious oxide remains as a white powder. The ortho-compound melts at  $145^{\circ}$ , and at a high temperature decomposes into arsenious oxide and a resinous mass, probably orthotritolylarsine. The para-compound melts at  $156^{\circ}$ , and at a higher temperature splits up into arsenious oxide and a substance crystallising in plates (m. p.  $130^{\circ}$ ), probably para-tritolylarsine. The oxides combine directly with chlorine and bromine to form tolylarsenious oxychlorides,  $\text{C}_6\text{H}_4\text{Me.AsOCl}_2$ , and oxybromides,  $\text{C}_6\text{H}_4\text{Me.AsOBr}_2$ .

The *monotolylarsinic acids*,  $\text{C}_7\text{H}_7\text{.AsO}_3\text{H}_2$ , produced by the action of water on the oxy- and tetra-chlorides, crystallise in needles or prisms, which are soluble in water and alcohol, but are insoluble in ether. The orthotolylarsinic acid is converted into the anhydride by being heated at its melting point ( $159^{\circ}$ ) for some hours. This acid forms an amorphous *silver* salt,  $\text{C}_7\text{H}_7\text{.AsO}_3\text{Ag}_2$ . The *barium* salt  $(\text{C}_7\text{H}_7\text{.AsO}_3\text{H})_2\text{Ba}$  does not form well defined crystals. When ammonia is added to a cold solution of calcium chloride and orthotolylarsinic acid, no change



takes place, but on heating the mixture a crystalline precipitate of  $(C_7H_7.AsO_3)Ca$  is deposited. The para-acid passes into the anhydride at  $113^\circ$ , and may be heated to  $300^\circ$  without melting. It forms a non-crystalline potassium salt; the silver salt becomes crystalline when boiled with dilute alcohol. The *barium* salt,  $(C_7H_7.AsO_3H)_2Ba$ , is deposited from an aqueous solution in anhydrous needles. The *calcium* salt,  $(C_7H_7.AsO_3H)_2Ca$ , is obtained in anhydrous plates on the addition of ammonia to a hot mixture of calcium chloride and paratolylarsinic acid. The copper and lead salts are insoluble in water.

W. C. W.

**Acridine.** By C. GREBE and H. CARO (*Ber.*, 13, 99—103).—By the oxidation of acridine with potassium permanganate solution, care being taken to avoid the presence at any time of an excess of the latter, the authors have obtained an acid which they term acridinic acid. It separates from hot saturated aqueous solutions in thin long needles of the composition  $C_{11}H_7NO_4 + 2H_2O$ . It is sparingly soluble in cold water, more easily in hot. When warmed with water in quantities insufficient to dissolve it, the needle-shaped crystals form brown tables, which contain 1 mol. of water of crystallisation. At  $120$ — $130^\circ$  acridinic acid loses both molecules of water of crystallisation and also carbonic anhydride, forming a monobasic acid,  $C_{10}H_7NO_2$ . Acridinic acid is dibasic, it crystallises from hydrochloric acid and platinum chloride as the free acid. When distilled with slaked lime, it yields quinoline as chief product: hence acridinic acid is quinoline-dicarboxylic acid,  $C_9H_7N(COOH)_2 + 2H_2O$ .

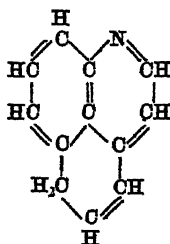
Acridinic acid at  $120$ — $130^\circ$  is resolved into carbonic anhydride and quinolinecarboxylic acid,  $C_9H_7NO_2$ , which crystallises in small ill-defined tables; it melts at  $275^\circ$ , is easily soluble in alcohol, soluble in hot water, but only sparingly in the cold. It forms salts with acids and bases, and yields quinoline on distillation.

The *silver* salt,  $C_9H_7N.COOAg$ , crystallises in small colourless prisms, very sparingly soluble in cold, more easily in hot water.

Its *copper* salt,  $(C_9H_7N.COO)_2Cu$ , forms a greenish-blue precipitate.

The *platinochloride*  $(C_{10}H_7NO_2.HCl)_2PtCl_4$ , crystallises from water, in which it is easily soluble, in reddish-yellow tables. The properties of this acid show it to be different from Weidel's cinchoninic acid (*Annalen*, 173, 84).

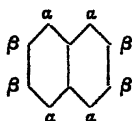
From the above, it is seen that acridine is a quinoline derivative, and for it the authors propose the following constitutional formula—



Acridine is attacked by the long-continued action of chromic and

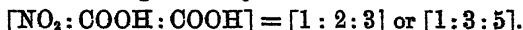
acetic acids; the same product being obtained if a solution of acridine in glacial acetic acid be treated with potassium permanganate. The product has neither basic nor acid properties, and the authors regard it as a ketone having the composition  $C_{12}H_7NO$ . It crystallises from acetic acid in yellow needles; it does not melt at  $320^\circ$ , but sublimes. It is soluble in acids and alkalis, dissolving in concentrated sulphuric acid with a yellow colour. P. P. B.

**The  $\alpha$ - and  $\beta$ -Positions in Naphthalene.** By F. REVERDIN and E. NOLTING (*Ber.*, 13, 36—38).—In support of the present view that the  $\alpha$ - and  $\beta$ -positions in naphthalene are the following—



the authors advance the following argument.

Beilstein and Kurbatow (*Ber.*, 12, 688) have shown that by the oxidation of  $\alpha$ -nitronaphthalene, a nitrophthalic acid is obtained, melting at  $212^\circ$ . According to theory, two such acids can exist, viz.:



O. Miller (*Ber.*, 9, 1191) has prepared a nitrophthalic acid melting at  $165^\circ$ , which he shows to correspond with the oxyphthalic acid of Baeyer. Further, Schall (*Ber.*, 12, 816) has shown that this oxyphthalic acid has the constitution:  $[OH : COOH : COOH] = [1 : 3 : 5]$ .

Hence the nitrophthalic acid, m. p.  $165^\circ$ , has the constitutional formula  $[1 : 3 : 5]$ , whilst the acid melting at  $225^\circ$  corresponds with the formula  $[1 : 2 : 3]$ , and as this corresponds with  $\alpha$ -nitrophthalene, the  $\alpha$ -position is adjacent to the carbon atom common to the two nuclei. P. P. B.

**Diphenyldiimidonaphthol.** By B. GÖRS (*Ber.*, 13, 123—125). *Diphenyldiimidonaphthol*,  $C_{16}H_8(NPh_2)_2.OH$ , is prepared by heating a mixture of equal parts of aniline and diimidonaphthol hydrochloride, until the evolution of ammonia ceases. The excess of aniline is removed from the crude product by distillation in a current of steam; the residue is extracted with boiling water and then purified by recrystallisation from alcohol and treatment with animal charcoal. Pure diphenyldiimidonaphthol crystallises in red needles which dissolve freely in benzene and ether, but are sparingly soluble in alcohol. The crystals melt at  $182^\circ$ , and can be sublimed without undergoing decomposition. The platinumchloride crystallises in brown plates insoluble in water but soluble in alcohol.

Similar compounds are obtained by the action of ortho- and para-toluidine on diimidonaphthol hydrochloride. W. C. W.

**The Third Anthracenecarboxylic Acid.** By C. LIEBERMANN and A. BISCHOF (*Ber.*, 13, 47—50).—Of the three anthracenecarboxylic acids two have been prepared, one from anthracene and carbonic chloride (Graebe and Liebermann), the second from an anthracene-

sulphonic acid by distillation with potassium ferrocyanide (Liebermann and v. Rath). The third acid has been obtained from an anthracenesulphonic acid obtained by the reduction of a commercial anthraquinonesulphonic acid with hydriodic acid. The anthracenesulphonic acid so obtained was distilled with potassium ferrocyanide, and the resulting nitrile saponified by means of alcoholic potash. The acid is obtained as a flocculent precipitate by acidifying the solution of the potassium salt; it consists of a mixture of two isomerides, which were separated by means of the different solubilities of their barium salts.

The acid from the soluble barium salt is identical with that prepared by Liebermann and v. Rath; the acid from the insoluble barium salt forms the greater portion of the mixture. This new *anthracene-carboxylic acid* has a brownish colour, is less soluble in alcohol and glacial acetic acid than the isomeride; it sublimes in leaflets and needles, and melts at about  $280^{\circ}$  without decomposition.

The *sodium* salt,  $C_{14}H_9COONa$ , is soluble in cold water, but is precipitated in spangles by boiling; its aqueous solutions are fluorescent.

The *ammonium* salt loses ammonia on evaporation, its solutions yield flocculent precipitates with barium chloride, ferric chloride, lead acetate, and copper acetate. The *barium* salt is slightly soluble in hot water.

The *ethyl* salt,  $C_{14}H_9COOEt$ , is easily soluble in alcohol, melts at  $134^{\circ}$ , and distils without decomposition.

This new anthracenecarboxylic acid, like the one described by Liebermann and v. Rath, yields an anthraquinonecarboxylic acid,  $C_{14}H_7O_2COOH$ , on oxidation. It crystallises from glacial acetic acid in long, light yellow needles, melting at  $285^{\circ}$ , like its isomeride, from which it is distinguished by the insolubility of its barium salt. The solution of its alkaline salts do not fluoresce. With zinc-dust and soda, it yields the characteristic red coloration, distinguishing all uncoloured anthraquinone derivatives from those of anthracene.

The authors conclude that the carboxyl group in the new anthracenecarboxylic acid occupies the same position as the hydroxyl in oxyanthraquinone. Since the sulphonic acid from which it was prepared yields chiefly oxyanthraquinone on fusion with potash, the formation of the second carboxylic acid is probably due to the presence of a sulphonic acid which yields erythroxyanthraquinone on fusion with potash. The sulphonic acid used in this investigation is the one prepared for the manufacture of alizarin.

P. P. B.

**Fluoranthene, a New Hydrocarbon from Coal-tar.** By R. FITTIG and H. LIEPMANN (*Annalen*, 200, 1—21).—The preparation of this hydrocarbon from the crude mixture of pyrene, fluoranthene, &c., by crystallisation of their picric acid compounds, is much facilitated by a previous fractional distillation under reduced pressure. Pure fluoranthene boils at  $250$ — $251^{\circ}$  under 60 mm. pressure, at  $217^{\circ}$  under 30 mm.; pure pyrene at  $260^{\circ}$  under 60 mm. The portion boiling between  $240^{\circ}$  and  $250^{\circ}$  under 60 mm. may be treated as already described (*Annalen*, 193, 142). The vapour-density of the hydrocarbon corresponds with the formula  $C_{16}H_{10}$ .

As previously mentioned, chromic mixture oxidises fluoranthene into diphenylene-ketone-carboxylic acid and a quinone which is only produced in small quantity. By suitably moderating the reaction, the acid, quinone, and unaltered hydrocarbon are obtained together as an insoluble deposit. The acid may be extracted from the mixture by sodium carbonate, and on crystallising the residue from hot alcohol and washing the crystals with light petroleum to remove adhering hydrocarbon, a compound of the quinone with fluoranthene was obtained,  $C_{18}H_{12}O_2 + 2C_{16}H_{10}$  (m. p.  $102^\circ$ ). Repeated crystallisation from alcohol resolves it partially into its constituents; hydrogen sodium sulphite decomposes it at once. The quinone crystallises in red needles (m. p.  $188^\circ$ ).

Treatment with chromic mixture converts this quinone completely, and apparently directly, into carbonic acid and water; it is not therefore a product intermediate between the hydrocarbon and diphenylene-ketone-carboxylic acid, but may be formed along with the latter, which is exceedingly stable towards oxidants. In virtue of this stability, the acid may be readily obtained from the crude mixture of pyrene and fluoranthene. 100 grams of hydrocarbon are treated with 600 grams of dichromate and 1000 grams of sulphuric acid diluted with five times its volume of water, and the mixture slowly heated to boiling, avoiding too violent an action. From the powdered and washed deposit, the acid may be extracted by sodium carbonate, precipitated by hydrochloric acid, and boiled with barium carbonate and animal charcoal. From the solution thus obtained, hydrochloric acid precipitates it in a nearly pure state.

Fuming nitric acid dissolves this acid on gentle heating, and on cooling deposits nitrodiphenylene-ketone-carboxylic acid,  $C_{14}H_7(NO_2)O_3$ , in long yellow needles, which may be purified by conversion into the barium salt. The nitro acid crystallises from alcohol in brilliant golden-yellow needles (m. p.  $245-246^\circ$ ) which are insoluble in water, but dissolve in glacial acetic acid. Its barium salt was analysed.

The conversion of diphenylene-ketone-carboxylic acid into isodiphenic acid, and the various salts of the latter, have been already described. Analyses of the free acid are now given. Its *methyl* salt,  $C_{12}H_5(COOCH_3)_2$  (m. p.  $69.5^\circ$ ), and its *ethyl* salt (an uncrystallisable syrup) are obtained by the action of sulphuric acid on solutions of the acid in the corresponding alcohols. Isophenic acid is easily oxidised, yielding isophthalic acid in theoretical quantity, together with carbonic acid and water. By this behaviour, it is distinguished from its isomeride diphenic acid, which yields only carbonic acid and water (Hummel, *Annalen*, 193, 130). Its general characters also distinguish it from its other isomeride diphenyl-dicarboxylic acid (Doebner, *Annalen*, 172, 117).

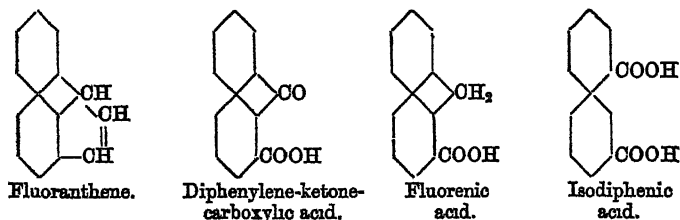
When treated with nascent hydrogen (from sodium amalgam), diphenylene-ketone-carboxylic acid passes into a carboxyl derivative of

fluorene (diphenylene-methane), 
$$\begin{array}{c} C_6H_5 \\ | \\ C_6H_5-CH_2-COOH \end{array}$$
 which the authors

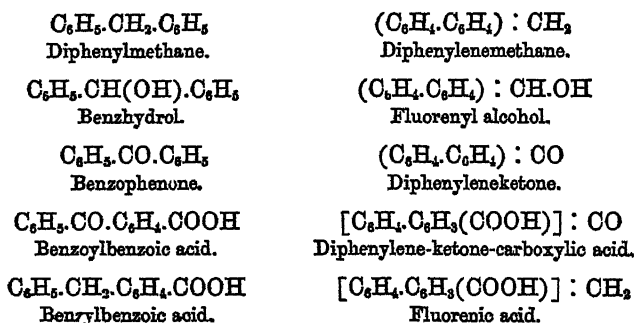
name *fluorenic acid* (m. p.  $245-246^\circ$ ). The new acid is scarcely soluble in boiling water, but easily in hot alcohol; it may be sublimed

unchanged. Barium and calcium salts and a crystalline ethyl salt (m. p. 53.5°) were prepared. The acid yields fluorene with the greatest ease when distilled with lime. Chromic mixture destroys it completely, but potassium permanganate in alkaline solution reconverts it into diphenylene-ketone-carboxylic acid. It is isomeric with Friedländer's fluorene-carboxylic acid (*Ber.*, 10, 537) obtained by reduction of diphenylene glycollic acid.

Isodiphenic acid decomposes so easily into diphenylene-ketone and carbonic anhydride, that one of its carboxyl-groups must be in the ortho-position with respect to the point of union of the two benzene nuclei; and since it yields isophthalic acid by oxidation, the second carboxyl-group must occupy the meta-position in the second nucleus. The latter position must also be assigned to the carboxyl-groups of the closely allied diphenylene-ketone-carboxylic and fluorenic acids. The constitution of fluoranthene having been previously ascertained (*Annalen*, 193, 142), the relationship of these bodies may be exhibited as follows:—



Finally, the author points out the parallelism between the derivatives of diphenylmethane and fluorene:—



Ch. B.

**Changes produced by Hydration and Dehydration in the Lævorotary Terpene from French Turpentine Oil.** By F. FLAWITZKY (*Ber.*, 12, 2354—2359).—*Lævorotary terpene hydrate*,  $C_{10}H_{18}O$ , is obtained by treating the rectified lævorotary terpene from French turpentine oil with a mixture of  $1\frac{1}{2}$  parts of alcohol (90 per cent.) and  $\frac{1}{2}$  part of sulphuric acid (sp. gr. 1.64°). After removal of the undissolved terpene the colourless solution is decom-

posed with water and fractionated in a current of steam, and finally distilled, the portion boiling at 211—215° being collected. This terpene hydrate boils at 218—221° (corr. bar. 766·3 mm.), and its action on polarised light is represented by  $\alpha_D = -51·7°$ . Its coefficient of expansion between 0 and 18° =  $-0·00083$ , therefore  $[\alpha]_D = \frac{-51·7}{0·9201} = -56·2°$ .

(Sp. gr. at 0° 0·9339, and at 18° 0·9201.) It is insoluble in water, but dissolves in a mixture of alcohol and sulphuric acid, its optical activity being thereby diminished, and finally disappearing altogether; on distillation, it undergoes slight decomposition, leaving an almost colourless residue. The dihydrochloride alone is obtained by saturating the above hydrate with gaseous hydrochloric acid, when the liquid assumes a violet-red colour and the dichlorhydrate separates out in crystals (m. p. 49°). The alcoholic solution of this compound is optically inactive.

The application of the acetic anhydride reaction to lævorotary terpene hydrate, although not conclusive, appears to show that the latter body contains a hydroxyl-group. The more volatile portion of the product obtained by this reaction contains a new substance, viz., lævorotary isoterpene,  $C_{10}H_{18}$  (b. p. 179, corr.: bar. 762·6 mm.), which readily undergoes oxidation, so that after standing several days and being redistilled over sodium, it always yields a brown precipitate. It has a feeble odour, different from that of the terpene from turpentine oil. It dissolves in alcoholic sulphuric acid. The chief points of difference between this substance and ordinary lævorotary terpene are as follows:—

|                          | Terpene. | Isoterpene. |
|--------------------------|----------|-------------|
| Boiling point .....      | 155°     | 179°        |
| $[\alpha]_D$ .....       | — 43·4   | — 61·0°     |
| Sp. gr. at 0° .....      | 0·8749   | 0·8639      |
| „ at 20° .....           | 0·8587   | 0·8486      |
| Coefficient of expansion | 0·00096  | 0·00091     |

On treatment with gaseous hydrochloric acid, the terpene of b. p. 155° gives only the solid monochlorhydrate, the liquor remaining colourless, whereas the new terpene of b. p. 179° gives the crystalline dichlorhydrate, the liquid at the same time becoming red. The author considers that the presence of moisture plays an important part in the formation of the dihydrochloride, which is readily converted into terpene hydrate on treatment with water. In many respects lævorotary isoterpene resembles the terpene from essence of elemi and that from oil of citron, but the former has a larger lævorotary power whilst the latter is dextrorotary.

T. C.

**Compounds in Animal Tar.** By H. WUIDEL and G. L. CIAMICIAN (*Ber.*, 13, 65—85).—II. *The Non-basic Constituents.*—The material used in this investigation was obtained from bone-oil by shaking it up with dilute acid and then separated by distillation into the following fractions:—I. 98—150°; II. 150—220°; III. 220—360°. Each fraction was then boiled with solid potash until the evolution of

ammonia ceased, and was thus separated into potassium salts of fatty acids, an aqueous portion, and an oil consisting of hydrocarbons.

I. The potassium salts of this fraction yielded the following acids:—Propionic, normal butyric, pantoic, and isocaproic acids. The aqueous portion contained valeramide. The oil was further separated into two fractions, one boiling at 110–130°, and the other at 130–180°.

The first yielded toluene, ethylbenzene, and pyrroline, which boils at 126·2° (bar. 746·5 mm.) and not at 133°, as usually stated; its sp. gr. is 0·9752 at 12·5°. The authors also confirm the observation of Anderson as to the formation of pyrrol-red, but are unable to attribute to it a definite composition.

The higher fraction yielded some pyrroline and three hydrocarbons:—Metadihydroethylbenzene,  $C_9H_{14}$ , a colourless mobile liquid, of sweet ethereal odour, and boiling at 153·5° (bar. 748·7 mm.); on oxidation it forms isophthalic acid. Metadihydromethylcymene,  $C_{10}H_{16}$ , a colourless liquid, having an odour resembling that of turpentine, and boiling at 165·5° (bar. 748·8 mm.); oxidising agents convert it into isophthalic acid. It forms an addition compound with bromine, which, when heated in sealed tubes at 180° with aniline, yields an isomeride of cymene, boiling at 174–175°. The third hydrocarbon, which has also the composition  $C_{10}H_{16}$ , boils at 172·5° (bar. 748·5 mm.), and yields isophthalic acid on oxidation.

The fraction II, when similarly treated, yielded isocaproic acid, phenol, two homologues of pyrroline, naphthalene, and a hydrocarbon,  $C_{11}H_{18}$ .

*Homopyrroline*,  $C_4H_7MeNH$ , is a colourless liquid with an odour resembling that of chloroform, and boiling at 145·5° (bar. 742·8 mm.). Its properties are similar to those of pyrroline, but it is attacked by acids less easily than the latter; it forms a white curdy precipitate with mercuric chloride. The acetyl derivative,  $C_4H_7MeN\dot{A}c$ , forms a crystalline mass (m. p. 4–6°).

*Dimethylpyrroline*,  $C_4H_7Me_2NH$ , the second homologue of pyrroline, is an almost colourless liquid of a somewhat disagreeable odour (b. p. 164°, bar. 792 mm.). Its acetyl derivative,  $C_4H_7Me_2N\dot{A}c$ , is a viscous, almost colourless liquid, slightly soluble in water, and remaining liquid at –20°.

An isomeride of homopyrroline has been described by Bell (*Ber.*, 9, 935, and 10, 1861); it is methylpyrroline,  $C_4H_7NMe$ .

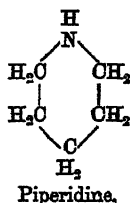
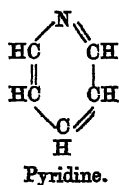
The hydrocarbon,  $C_{11}H_{18}$ , is a colourless, strongly refractive liquid (b. p. 162°). It does not combine with hydrochloric acid, and on oxidation yields a small quantity of isophthalic acid. A small quantity of an isomeride of this body has been also obtained from this fraction; it boils at 202–203°.

III. This fraction yielded chiefly palmitic and stearic acids.

P. P. B.

**Conversion of Piperidine into Pyridine.** By W. KENIGS (*Ber.*, 12, 2341–2344).—On heating piperidine,  $C_6H_{11}N$ , for several hours at 300° with concentrated sulphuric acid, it is oxidised to pyridine. The same result is obtained, although not so readily, by heating an aqueous solution of piperidine with silver oxide. Hofmann (*Ber.*, 12, 984) has previously shown that a body having the composition of dibromoxy-

pyridine,  $C_5H_5BrNO$ , is obtained when piperidine hydrochloride is treated with an excess of bromine at  $200-220^\circ$ , but he was unable to prepare this compound directly from pyridine. These facts show that the alkaloid from pepper is a derivative of pyridine. The author considers that the oxidation of piperidine to pyridine is analogous to the behaviour of aromatic hydro-derivatives, in which the double attachments in the benzene ring are changed to single ones by addition of hydrogen, and which on oxidation lose these hydrogen atoms, and are again converted into compounds with double attachments. So far, however, it has not been possible, from want of material, to convert pyridine back into piperidine. The following formulæ show the relation between pyridine and piperidine:—



Now, since piperine on boiling with potash gives piperidine and piperinic acid, it may be considered as piperonyl-piperidine,



and is, therefore, analogous to the corresponding benzoyl-compound. As the constitution of the two radicles,  $C_5H_{10}N$  (*vide supra*), and  $CO.C_{11}H_8NO_2$  (Fittig), has already been determined, we know that of piperine, which is therefore the first alkaloid of which the constitution is known with comparative certainty.

Experiments are in progress with the object of obtaining pyridine synthetically from the ethyl-allylamine isomeric with piperidine, by a reaction analogous to that by which quinoline has been obtained from allylaniline (Koenigs, *Ber.*, 12, 453).

T. C.

**Pyridinecarboxylic Acids.** By S. HOOGWERFF and W. A. v. DORP (*Ber.*, 13, 61—65).—Pyridinetricarboxylic acid, obtained by oxidation of quinine (this Journal, 1879, Abst., 541) when heated at  $185-190^\circ$ , is resolved into carbonic anhydride and *pyridinedicarboxylic acid*. Pyridine-dicarboxylic acid crystallises from water in needles; it melts with decomposition at  $250^\circ$ ; is sparingly soluble in alcohol, ether, and benzene; with ferrous sulphate it gives no coloration. The properties of this acid show that it is identical with the cinchomeronic acid described by Weidel and v. Schmidt (*ibid.*, 1879, 947). The authors attribute to the barium salt the formula  $C_7H_5NO_4Ba + 1\frac{1}{2}H_2O$ , and to the calcium salt  $C_7H_5NO_4Ca + 3\frac{1}{2}H_2O$ . Besides the silver salt,  $C_7H_5NO_4Ag$ , described by Weidel and Schmidt, the authors obtain an acid salt,  $C_7H_4NO_4Ag$ , by treating the aqueous solution of the acid with silver nitrate, as a white crystalline precipitate. The aqueous solution of the acid in presence of acetic acid gives with copper acetate a light blue



cloud, which increases on heating and disappears when the solution cools. The identity of this pyridinedicarboxylic acid with cinchomeronic acid is further shown by the fact that it also yields a pyrocinchonic acid (m. p. 94—97°); Weidel and v. Schmidt found the m. p. to be 90°.

This pyridinedicarboxylic acid is resolved by heat into carbonic and *pyridenemonocarboxylic acid*, which crystallises from water in nodules. This acid the authors style pyrocinchomeronic acid; it is sparingly soluble in water and alcohol, and very slightly in ether and benzene; its aqueous solutions yield no coloration with ferrous sulphate. The *hydrochloride*,  $C_6H_4NO_2.HCl$ , forms large shining crystals. The *platinochloride*,  $(C_6H_4NO_2)_2.2HCl.PtCl_4 + 2H_2O$ , forms red crystals, resembling the corresponding salt of nicotinic acid.

Beside this pyridenemonocarboxylic acid, a small quantity of an acid, apparently nicotinic acid, is formed at the same time.

The acid obtained by the authors from quinoline (this Journal, Abst., 1879, 731) and described as pyridinedicarboxylic acid, has proved on further investigation to be nicotinic acid.

The three possible pyridinecarboxylic acids are now known, viz., pyrocinchomeronic, nicotinic, and picolinic acids (Weidel, *Ber.*, 12, 1989). And of the six possible pyridinedicarboxylic acids, five are already known, viz. (1), the  $\alpha$ -acid (Dewar, *Zeit. f. Chem.*, 1871, 116), (2) the  $\beta$ - and  $\gamma$ -acids (Ramsay, this Journal, Trans., 1879, 289), the fourth is cinchomeronic acid, and, finally, the fifth acid is that obtained from quinoline by the authors (*loc. cit.*). P. P. B.

**Pyridinetricarboxylic Acid from Cinchona Alkaloids.** By S. HOOGEWERFF and W. A. v. DORP (*Ber.*, 13, 152—154).—The acid obtained by the oxidation of quinine, quinidine, cinchonine, and cinchonidine, by potassium permanganate is identical with the pyridinetricarboxylic acid,  $C_6H_3NO_6 + 1\frac{1}{2}H_2O$ , which Skraup (*Ber.*, 12, 2331) prepared from cinchonic acid. The acid is soluble in 83.1 parts of water at 15°. The solution is optically inactive. The metallic salts have the following composition:— $(C_6H_3NO_6)_2Ba_3 + 16H_2O$ ;  $(C_6H_3NO_6)_2Ca_3 + 14H_2O$ ;  $C_6H_3Ag_3NO_6 + 2H_2O$ ;  $C_6H_3Ag_2NO_6 + H_2O$ ;  $C_6H_3AgNO_6 + C_6H_3NO_6 + H_2O$ , and  $C_6H_3K_3NO_6 + 3H_2O$ . W. C. W.

**Synthesis of the Homologues of Hydrocarbostyryl and Quinoline.** By A. BAER and O. R. JACKSON (*Ber.*, 13, 115—123).—By the action of sodium-amalgam on phenylangelic acid (prepared from normal butyric acid and benzaldehyde) *sodium phenylethylpropionate* is obtained. The free acid,  $CH_2Ph.CHEt.COOH$ , is an oil which boils at 272°, and does not solidify in a freezing mixture. The silver salt is amorphous and insoluble in water; the barium salt dissolves freely in water, but is not crystalline.

*Ethylhydrocarbostyryl*,  $C_6H_4 \begin{matrix} \swarrow CH_2.CHEt \\ \searrow NH.CO \end{matrix}$ , formed by treating nitrophenylethylpropionic acid with tin and hydrochloric acid, dissolves freely in alcohol, ether, and benzene, and is sparingly soluble in hot

water. It dissolves easily in strong acids, but is reprecipitated on the addition of water. The crystals melt at  $88^{\circ}$ ; if they are heated again soon after solidification, the melting point falls to  $76^{\circ}$ , but gradually rises if the specimens are kept for some time at the ordinary temperature.

*Ethylchloroquinoline*,  $C_8H_7$   $\begin{matrix} \text{CH} : \text{CEt} \\ | \\ \text{N} : \text{CCl} \end{matrix}$ , m. p.  $72^{\circ}$ , is produced by the

action of phosphorus pentachloride on ethylhydrocarbostyryl. It is a weak base, sparingly soluble in water, but dissolving freely in other solvents.

The platinochloride is soluble in alcohol, but is decomposed by water. In the preparation of the chloroquinoline, ethylcarbostyryl (m. p.  $168^{\circ}$ ) appears to be formed as a bye-product.

$\beta$ -*Ethylquinoline*,  $C_8H_7$   $\begin{matrix} \text{CH} : \text{CEt} \\ | \\ \text{N} : \text{CH} \end{matrix}$ , is obtained by acting on ethyl-

chloroquinoline with a solution of hydriodic acid in acetic acid, rendering the product alkaline, and distilling off the base in a current of steam. The free base resembles quinoline; the platinochloride is insoluble in alcohol, and less soluble in water than the corresponding quinoline compound.

Hydrocinnamylacrylic acid, previously obtained by Perkin (this Journal, 1877, i, 405) by the reduction of cinnamylacrylic acid with sodium-amalgam as an oily liquid, solidifies in a freezing mixture, forming colourless plates (m. p.  $29^{\circ}$ ). The acid combines directly with bromine in a carbon bisulphide solution, with production of an addition-product (m. p.  $109^{\circ}$ ), crystallising in prisms, which are soluble in light petroleum and in chloroform. It also combines directly with hydrobromic acid. When hydrocinnamylacrylic acid is treated with a solution of hydriodic acid in acetic acid at  $160^{\circ}$ , and the product diluted with water and mixed with sulphurous acid, normal *phenylvaleric acid* separates out as an oily liquid which solidifies, forming rhombic plates (m. p.  $59^{\circ}$ ) sparingly soluble in water. The barium salt of this acid is slightly soluble, and the silver salt insoluble in water.

Nitrophenylvaleric acid on reduction with tin and hydrochloric acid, does not yield a derivative analogous to hydrocarbostyryl.

W. C. W.

**Action of Benzoic Chloride on Morphine.** By K. POBSTORFF (Ber., 13, 98—99).—By the action of benzoic chloride on morphine free from water, in sealed tubes at  $109$ — $110^{\circ}$ , tribenzoylmorphine,  $C_{17}H_{18}NO_3\bar{B}z_3$ , is obtained; it forms large, colourless, columnar crystals (m. p.  $186^{\circ}$ ). It is insoluble in water, sparingly soluble in cold alcohol, more easily in hot alcohol. It has no basic properties. By the action of benzoic acid and benzoic anhydride on morphine, Beckett and Wright (this Journal, 28, i, 23) obtained monobenzoylmorphine,  $C_{17}H_{18}NO_2\bar{B}z$ , and dibenzoylmorphine,  $C_{17}H_{17}NO_2\bar{B}z_2$ , respectively, to which bodies they attribute basic properties.

The author concludes that as morphine is a nitril base, as shown by the preparation of methylmorphine hydroxide, therefore there is

no hydrogen combined directly with the nitrogen, so the benzoyl compounds indicate the existence in morphine of three hydroxyl-groups.

P. P. B.

**Action of Potassium Ferricyanide on Morphine.** By K. POLSTORFF (*Ber.*, 13, 86—88).—The action of an alkaline solution of potassium ferricyanide on morphine, observed by Kieffer (*Annalen*, 103, 254), converts it into oxydimorphine, thus:  $2C_{17}H_{19}NO_3 + 2KHO + 2K_3Fe(CN)_6 = 2H_2O + 2K_4Fe(CN)_6 + C_{34}H_{38}N_2O_6$ .

*Oxydimorphine* is obtained by precipitating its hydrochloric acid solution with ammonia as a colourless heavy crystalline powder. It is insoluble in ordinary solvents, and is precipitated from the solution of its salts by caustic alkalis, but is soluble in excess; on warming its solution in aqueous ammonia, it is precipitated. *Oxydimorphine* has the composition  $C_{34}H_{38}N_2O_6 + 3H_2O$ .

*Oxydimorphine sulphate*,  $C_{34}H_{38}N_2O_6.H_2SO_4 + 8H_2O$  forms small, concentrically-grouped needles, sparingly soluble in cold, more easily in hot water.

*Oxydimorphine hydrochloride*,  $C_{34}H_{38}N_2O_6.2HCl + (?H_2O)$ , is a shining white, indefinitely crystalline powder. It is easily soluble in water; the addition of acid lessens its solubility. Preparations have been obtained with varying amounts of water of crystallisation, e.g., with  $6\frac{1}{2}$  mols., 1 mol., and 2 mols. of water.

P. P. B.

**Schützenberger's Oxymorphine** (*Ber.*, 13, 88—90); **Action of Potassium Permanganate on Morphine** (*Ber.*, 13, 91); **Action of Atmospheric Oxygen on Morphine in Ammoniacal Solution** (*Ber.*, 13, 92—93). By K. BROCKMANN and K. POLSTORFF. The oxymorphine prepared by Schützenberger (*Bull. Soc. Chim.*, 1865, 176) by the action of silver nitrite and hydrochloric acid on morphine, to which he ascribed the formula  $C_{17}H_{19}NO_4$ , is found to be identical with oxydimorphine,  $C_{34}H_{38}N_2O_6$ , prepared from morphine by the action of potassium ferricyanide; its formation may be expressed as follows:  $2C_{17}H_{19}NO_3.HCl + AgNO_2 = C_{34}H_{38}N_2O_6 + 2AgCl + 2H_2O + 2NO$ .

The authors find that oxydimorphine is formed when morphine is oxidised by means of potassium permanganate in presence of an alkaline carbonate.

The authors find that oxydimorphine is also obtained when an ammoniacal solution of morphine is exposed to the air. The identity of the base in each of the above instances with that obtained by the action of potassium ferricyanide on morphine is shown not only by its properties but also by those of its sulphate and hydrochloride.

P. P. B.

**Methylmorphine Hydroxide.** By K. BROCKMANN and K. POLSTORFF (*Ber.*, 13, 96—98).—*Methylmorphine hydroxide* is obtained by first converting the iodide into sulphate by means of silver sulphate, and then heating the sulphate with baryta-water. After removing the excess of baryta by carbonic anhydride, the filtrate was concentrated to a syrup, taken up with alcohol, and from the alcoholic solution the hydroxide was precipitated by ether in the form of brittle yellow

needles, having the composition  $C_{17}H_{19}NO_3 \cdot CH_3OH + 5H_2O$ . It is very soluble in water, the aqueous solution decomposes on exposure to the air, forming coloured uncrystallisable products. P. P. B.

**Action of Potassium Ferricyanide on Methymorphine Iodide.** By K. POLSTORFF (*Ber.*, 13, 93—96).—Methymorphine, when oxidised by potassium ferricyanide in an alkaline solution, yields the basic iodide of methyloxydimorphine, thus:  $2C_{17}H_{19}NO \cdot CH_3I + 2K_3Fe(CN)_6 + 3KOH = (C_{17}H_{18}NO_3)_2 \cdot CH_3I \cdot CH_3OH + 2K_4Fe(CN)_6 + KI + 2H_2O$ .

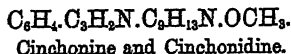
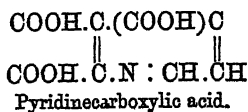
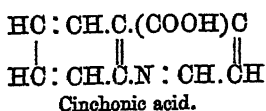
*Basic methyloxydimorphine iodide*,  $(C_{17}H_{18}NO_3)_2 \cdot CH_3I \cdot OH + 5H_2O$ , is obtained by treating its solution in hydrochloric acid with ammonia. It forms small colourless tablets, easily soluble in hot and sparingly soluble in cold water: its aqueous solutions have an alkaline reaction. The neutral iodide,  $(C_{17}H_{19}NO \cdot CH_3I)_2 + 4H_2O$ , is obtained by treating the basic iodide with hydriodic acid; it forms small yellow quadratic prisms. It is sparingly soluble in cold, and easily in hot water. It is also prepared by heating the basic iodide with methyl iodide in sealed tubes at  $125^\circ$ .

The *neutral sulphate*,  $(C_{17}H_{19}NO_3 \cdot CH_3O)_2SO_4 + 4H_2O$ , is obtained by treating the basic iodide with sulphuric acid, and then with a boiling solution of silver sulphate. It crystallises in yellowish, shining leaflets, easily soluble in hot water, but less easily in cold. By treating its concentrated solution with ammonia, the basic sulphate separates out in colourless shining scales.

*Methyloxydimorphine hydrazide*,  $(C_{17}H_{18}NO_3 \cdot CH_3OH)_2 + 7H_2O$ , cannot be prepared by treating the iodide with moist silver oxide, since oxidation takes place; but it is obtained by treating the sulphate with an excess of baryta-water and removing the excess of the latter by means of carbonic anhydride. The base is precipitated from its aqueous solutions by alcohol as an indistinctly crystalline powder. It is easily soluble in water, but insoluble in alcohol. P. P. B.

**Constitution of Cinchonine and Cinchonidine.** By Z. H. SKRAUP (*Annalen*, 201, 291—333).—The following conclusions were deduced from the results of the author's investigations on the oxidation products of cinchonine, cinchonidine, and cinchonic acid (*Ber.*, 11, 1516; 12, 230, 1107, 2231; *Annalen*, 197, 226, 352, and 374; and this Journal, 1879, Abstr., 71, 656, 810, 948). In the oxidation of chinoline and cinchonidine by chromic mixture, the methoxyl group is first attacked, with formation of formic acid and carbonic anhydride, probably of cinchotenine and cinchotenidine or closely allied compounds as intermediate products. Cinchonic (quinolinemonocarboxylic) acid,  $C_{10}H_7NO_2$ , and a non-crystalline acid which forms exceedingly hygroscopic salts, are the results of the reaction. Cinchonic acid is monobasic, and does not form acid salts as stated by Weidel (*Wien. Akad. Ber.*, 1874, Part II). On further oxidation it yields pyridine-tricarboxylic acid, which is identical with Weidel's oxycinchomeronic acid, and with the pyridine-tricarboxylic acid obtained by Hoogewerff and van Dorp (*Ber.*, 13, 152; this vol., p. 406), by the action of potassium permanganate on quinine, quini-

dine, cinchonine, and cinchonidine. The constitution of these acids and of cinchonine and cinchonidine may be represented by the following formulæ:—



The tricarboxylic acid decomposes when heated at its melting point, with evolution of carbonic anhydride and production of the dicarboxylic and  $\gamma$ -monocarboxylic acids. The latter acid melts at  $305^\circ$  and sublimes without decomposition.

W. C. W.

**Belladonnine.** By K. KRAUT (*Ber.*, 13, 165—166).—Commercial belladonnine appears to be a mixture of belladonnine and atropine, since, on boiling with baryta-water, atropic acid and tropine pass into solution, while the belladonnine remains undissolved. Belladonnine appears to be isomeric with atropine; it may possibly be identical with hyoscyamine.

W. C. W.

**Artificial Alkaloids.** By A. LADENBURG (*Ber.*, 13, 104—110).—In a former communication (this Journal, Abstr., 1879, 733), the author described the artificial preparation of atropine. Further experiments prove that atropine so prepared is chemically identical with natural atropine, and that this identity holds with regard to its physiological action. The author has prepared by similar reactions the following bases analogous to atropine.

*Salicyltropine*,  $\text{C}_{15}\text{H}_{19}\text{NO}_3$ , from tropine salicylate. It crystallises in white silky leaflets, sparingly soluble in water, but easily in alcohol, m. p.  $57-60^\circ$ . Its production is represented as follows:— $\text{C}_8\text{H}_{15}\text{NO} + \text{C}_7\text{H}_5\text{O}_3 = \text{C}_{15}\text{H}_{19}\text{NO}_3 + \text{H}_2\text{O}$ . It is a strong base; the hydrochloride crystallises from water in slender shining needles, the aqueous solutions giving a crystalline precipitate with platinum chloride. It forms a yellow crystalline aurochloride. Picric acid gives an amorphous precipitate, potassium mercuric iodide a white gelatinous precipitate, and tannic acid a white precipitate soluble in dilute acids. Solution of iodine in potassium iodide produces separation of a brown oil. Salicyltropine is a feeble poison, but has no action on the eye.

*Oxytoluytropine* or *homatropine* is obtained from tropine mandelate. It is purified either by means of the aurochloride or the picrate, from both of which the base is separated by treatment with potassium carbonate as an oil.

*Homatropine aurochloride*,  $\text{C}_{15}\text{H}_{21}\text{NO}_3.\text{HCl.AuCl}_4$ , forms first as an oil, which becomes crystalline on standing; it crystallises from water in prisms.

The *picrate*,  $\text{C}_{15}\text{H}_{21}\text{NO}_3.\text{C}_6\text{H}_3(\text{NO}_2)_3.\text{OH}$ , is obtained as an oil, which becomes crystalline; it is soluble in hot water, from which it crystallises in yellow shining leaflets.

The solutions of its hydrochloride yield no precipitate with tannic acid; with potassium mercuric iodide, a white curdy precipitate; with mercuric chloride, a white oil; and with iodine, yellow crystals and a black oil. In concentrated solutions platinum chloride gives an amorphous precipitate, the filtrate from which on concentration yields beautiful needles.

Homatropine acts on the pupil of the eye as energetically as atropine.

*Phthalyltropine*,  $C_{24}H_{22}N_2O_4$ , is obtained from tropine and phthalic acid. It forms white silky needles, sparingly soluble in water, but easily in alcohol, m. p.  $70^\circ$ . Its reactions are similar to those of atropine; its platinochloride crystallises in needles, and is sparingly soluble.

Hyoscyamine, which the author purified by means of the aurochloride, is isomeric with atropine, as shown by its analyses and those of the aurochloride. It crystallises in smaller and less well formed prisms than atropine, and melts at  $113.5^\circ$ , atropine melting at  $108.5^\circ$ . Its aurochloride,  $C_{17}H_{23}NO_5 \cdot HCl \cdot AuCl_3$ , crystallises from water in beautiful leaflets, which have a golden lustre on drying. It melts at  $154^\circ$ , whilst the atropine salt melts at  $185^\circ$ .

The author is engaged with the further study of hyoscyamine.

P. P. B.

**Erythroxyton Coca.** By D. F. SHULL (*Pharm. J. Trans.* [3], 10, 408).—The leaves of this plant, a native of South America, resemble those of the tea plant, have an astringent and aromatic taste, and produce a smarting and numbness of the tongue, due to the presence of an alkaloid, *cocaine*.

The leaves are exhausted with alcohol, the colouring matter precipitated with lime, and the filtered solution evaporated to a small bulk; water is then added, and the evaporation continued to expel the alcohol; after adding potassium carbonate, filtering, and saturating the solution with potassium carbonate, the alkaloid may be extracted by agitation with ether. The ethereal solution is decolorised with animal charcoal, and allowed to stand, when cocaine is obtained in colourless prismatic crystals, odourless, and of a bitter taste. It is soluble in alcohol, ether, chloroform, and water, has strong stimulating properties, produces a feeling of intoxication and a smarting and numbness of the tongue. A light brown amorphous substance is also obtained from the leaves, having a strong smell, a sharp burning taste, and an alkaline reaction. It is soluble in alcohol, ether, chloroform, and water. The leaves also contain gum, tannin, wax, and resin.

L. T. O'S.

**Baptisia Tinctoria.** By F. V. GREENE (*Pharm. J. Trans.* [3], 10, 584—585).—Failing to isolate the alkaloid of *Baptisia tinctoria*, either by the method of Smedley (*Am. J. Pharm.*, 1862, 310) or of J. A. Warner (*ibid.*, 1871, 251), the following method was adopted:—The powdered root is exhausted with water, the extract evaporated with calcined magnesia, the dried residue extracted with alcohol (95 per cent.), and the solution concentrated; distilled water is added, and filtered from precipitated resin. To the filtrate, tannic acid is added,

which precipitates the alkaloid; the precipitate is intimately mixed with lead oxide, dried, and exhausted with ether. On evaporating the solution a resinous mass is left, from which the pure alkaloid is separated by means of oleic acid at 100°. The oily solution is poured off and treated with benzin (? petroleum), which dissolves the oleate and excess of acid. This solution is shaken with water, acidulated with hydrochloric acid, and on standing acicular crystals separate out from the acid solution.

Octohedral crystals may be obtained by treating the root with sodium bicarbonate and evaporating the extract to dryness. The residue is exhausted with ether, the ether evaporated, the mass treated with water and filtered: after neutralising the aqueous solution with hydrochloric acid and extracting the colouring matter with ether, the solution is allowed to crystallise.

The alkaloid gives a precipitate with Mayer's reagent, potassium iodo-iodide, potassium-cadmium iodide, phosphomolybdic acid, sodium phosphotungstate, tannic and picric acids. It is soluble in water, alcohol, and ether, but insoluble in benzene and chloroform.

L. T. O'S.

**Phytolaccin.** By T. E. CLAESSEN (*Pharm. J. Trans.* [3], 10, 566).—Phytolaccin, a crystalline substance contained in the seeds of pokeberries (*Phytolacca decandra*), is obtained in needle-shaped crystals by extracting the seeds with alcohol, distilling the extract, washing the residue with light petroleum, pulverising the dried residue, exhausting with ether, and evaporating the solution. It is purified by recrystallisation from alcohol. Phytolaccin is tasteless, colourless, soluble in ether, chloroform, and alcohol, sparingly soluble in light petroleum, insoluble in water, dilute acid, strong acetic and hydrochloric acid, soda solution, and ammonia. Concentrated sulphuric acid dissolves it with a brownish-yellow colour, changing to red when heated; and in warm nitric acid, it dissolves with a yellow colour. It is precipitated in a flocculent state by water from its alcoholic and ethereal solution. On ignition, it first melts, then chars. It leaves no residue when burnt, and contains no nitrogen.

L. T. O'S.

**Phytolacca Decandra.** By A. C. EHRHARD (*Pharm. J. Trans.* [3], 10, 426—429).—An ethereal extract of the powdered root was evaporated to dryness, and the residue exhausted with alcohol. The alcoholic solution was found to contain potassium, calcium, sulphuric acid, and a fat or wax. The residue left after treating the ethereal extract with alcohol contained a crystalline acid resin, soluble in sulphuric acid with an olive-green colour, changing to purple on heating, and to red on addition of nitric acid.

After exhaustion with ether the root was treated with alcohol, and the extract obtained yielded two crops of crystals; the first consisted of the potassium salt of an organic acid, and the second of cane sugar. The mother-liquor contained a resin and a substance, the reactions of which are described, but no conclusions arrived at.

L. T. O'S.

**Apiol.** By H. C. WHITNEY (*Pharm. J. Trans.* [3], 10, 585—586).—The method adopted by Joret and Homolle for preparing apiol does

not yield the pure substance but a mixture of apiol and guatin (oil of parsley). Pure apiol is obtained by distilling parsley seed with water, and saturating the distillate with sodium chloride, when all the volatile oil separates out, which corresponds very closely to the apiol of Joret and Homolle. The residue in the retort was filtered, and the solution on cooling yielded a large quantity of apiin. The residuary seed when treated with petroleum spirit gave 9.114 per cent. of a green fatty oil and resin; further quantities of oil and resin were separated by ether, the resin being separated by alcohol. The alcoholic extract gave on evaporation a greenish-brown oily liquid, lighter than water, and easily saponified by alkalis. The author has failed to isolate the parsley camphor described by E. v. Gerichten.

L. T. O'S.

**Colouring Matter of the Caryophyllaceæ.** By H. BISCHOFF (*Bied. Centr.*, 1879, 875).—The colouring matter of the Caryophyllaceæ has been spectroscopically examined, the appearances with maximum and minimum absorption, and the action of acids and alkalis noted. The same colouring matter appears to be present in all the members of the family.

E. W. P.

**Putrefaction-products of Albumin.** By E. and H. SALKOWSKI (*Ber.*, 13, 189—193).—In continuing their research (*Ber.*, 12, 648 and 1438, this Journal, 1879. *Abst.*, 659), the authors find that the acetic and benzoic series of acids may be best separated from the hydroxy-acids in the products of putrefaction, by distillation in a current of superheated steam. The non-volatile portion contains, besides the hydroxy-acids, a crystalline compound which melts at 161° with simultaneous decomposition into carbonic anhydride and skatole.

The quantity of parahydroxyphenylacetic acid, formed by the putrefaction of blood albumin and the hydrocinnamic acid from the putrefaction of flesh, is diminished by the presence of air during the process, whilst the amount of cresol is increased.

W. C. W.

**Guanidine, an Oxidation-product of Albumin.** By F. LOSSEN (*Annalen*, 201, 369—376).—In order to settle the disputed question of the formation of urea by the action of potassium permanganate on albumin, an aqueous solution of purified egg albumin was treated with a mixture of potassium permanganate and magnesium sulphate, until a permanent colour was imparted to the liquid. The magnesium sulphate was added with a view of keeping the solution feebly alkaline. After filtering the mixture and acidifying with dilute sulphuric acid, a bulky precipitate is thrown down; the filtrate contains *guanidine*, which Béchamp (*Journ. de Pharm.* [3], 31, 32) mistook for urea.

W. C. W.



## Physiological Chemistry.

**Digestion of Food by the Horse when at Work.** By E. v. WOLFF and others (*Bied. Cent.*, 1879, 827—835).—The result of the experiments on the digestion of food by the horse, when performing different amounts of work, was that the digestion of food is not influenced by muscular exertion. Comparing the amount of matter assimilated during the digestion of various foods by the horse and sheep, the following facts are arrived at:—The horse makes less use of hay than ruminants, the difference being 11—12 per cent.; but crude protein is equally digested in both horse and sheep. On the other hand, there is a wide difference as regards fibre; although the digestion of the non-nitrogenous extractive matter is more equal. Comparison of the digestive capacity for various kinds of hay shows that they are alike in both animals as regards the total organic matter; but as regards the various constituents, there is a difference, viz., with smaller absolute quantities of protein the difference is smaller; but in a few sorts which are difficult of digestion, the horse makes a better use of the protein than the sheep. There does not appear to be much difference between the digestibility of the fat and non-nitrogenous extract in either animal, but the opposite is the case as regards the fibre. Oats and beans and steeped maize are digested with like ease. Feeding the horse continuously with the same sort of hay appears to have no influence on the digestion of that food, whether it be given in large or in small quantities.  
E. W. P.

**Absorption of Food.** (*Dingl. polyt. J.*, 234, 486—489).—Nutrition, as is well known, has to solve two problems, viz.:—(1) to build up and sustain the organism, and (2) to introduce and utilise latent energy so as to preserve the actual forces of the body and its organs, i.e., production of heat, electricity, mechanical labour, &c. The albuminoids have to fulfil the first-named task, whilst all organic substances develop force in proportion to the latent energy liberated during their conversion in the organism. The non-nitrogenous substances which take a subordinate part in the building up of the body, and consequently possess the largest amount of latent energy, are mainly utilised for the production of the vital forces, the chief agent of which is animal heat.

In order to estimate the nutritive value of a food, it does not suffice to ascertain the amount of nitrogen and carbonic acid, or to know the quantity of albumin, fat, and carbohydrates contained therein; but it is necessary that we should know the amount of every nutritive principle really absorbed into the system. To form a correct opinion as to the absorption of these different principles, we must further consider the quantity necessary for the preparation of a diet, in order to obtain the proper proportions of nitrogen and carbon. Meat, eggs, and white bread form the most favourable diet, whilst maize, potatoes, and black bread may be included in this group. As a rule, fat is absorbed into the system with but little residue. Larger quantities of

fat appear to influence the utilisation of the carbohydrates. However, the absorption of the latter into the system is of great importance, since they represent the greater part of the dry substances in the food of most men. Vegetable diet, which generally is poor in nitrogen, gives excrements with more nitrogen than animal food.

In conclusion, it is stated that the causes of the differences in the absorption of alimentary principles contained in various food-stuffs have still to be explained more satisfactorily. D. B.

**Feeding Experiments with Pigs.** By E. v. WOLFF, W. v. FUNKE, and G. DITTMANN (*Bied. Centr.*, 1879, 835—841).—The results of the experiments in which the fattening values of potatoes and flesh-meal are compared, are as follows:—The amount of dry matter given caused the live weight to increase in five months from 27·2 to 89·2 kilos.; the mean daily increase per head was 0·403 kilo., when the mean daily feeding was 0·450 kilo. By a judicious mixture of flesh-meal and boiled potatoes, a larger amount of solid matter is retained than when potatoes alone, or with split peas, are given. Likewise the nourishing influence of a given quantity of dry matter, together with flesh-meal, is greater than without the latter. Young pigs fatten better on potatoes than older ones. Beyond a certain range, there is no advantage in using flesh-meal, as a like quantity of carbohydrates will do as well; the minimum ratio appears to be 1 of flesh-meal to 33 of potatoes. Beyond this, 4·78 kilos. of potatoes seem to do the work of 1 kilo. of flesh-meal. The ratio of flesh-meal to potatoes = 1 : 25 yields good results. It appears, then, that flesh-meal may with advantage be mixed with any food poor in albuminoids.

E. W. P.

**Activity of Bees.** By E. EULENMEYER and A. v. PLANTA-REICHENAU (*Bied. Centr.*, 1879, 841—844).—The points to be determined were, whether bees find honey and wax ready formed in flowers or not, and whether they alter, wholly or in part, these substances. Several specimens of honey were examined, and the pollen separated by mixing the honey with water and then filtering, and in the filtrate were determined the coagulable albumin, total nitrogen, ash, and phosphoric acid. Fresh honey appears to contain more water than old honey; the coagulable albumin represents only part of the total nitrogen. Of the remaining nitrogenous matter, a part is soluble in alcohol, a part insoluble; the proportions which these bear to one another are ·0208 : ·0337 : ·0236; the nectar of plants contains no albumin. The amount of wax in honey was determined by means of ether, the extract so obtained being treated with alcohol to remove oils; the purified wax melted at 60°C., and was present in varying quantities: ·1603 : ·0357 : ·0967 part per 100 dry substance. The presence of cane-sugar was microscopically detected, but is present only in small quantities; the greater portion which is at first collected having been changed into glucose by the saliva of the bees, and by the ferment contained in the pollen. The authors consider that the wax is produced by the bees from sugar.

E. W. P.

**Physiological Action of Borax.** By E. DE CYON and G. LE BON (*Bied. Centr.*, 1879, 868).—Cyon states that meat preserved by borax

is not diminished in its power of nourishing, and that the substitution of borax for salt greatly aids assimilation of food; whereas le Bon asserts that meat cured with borax is useless as a food; in fact, is harmful. E. W. P.

## Chemistry of Vegetable Physiology and Agriculture.

**Alkaloid of *Lupinus Luteus*.** By H. C. SCHULZ (*Bied. Centr.*, 1879, 874).—The recognition of an alkaloid in lupines will account for the several fatal results of feeding cattle with them. In the seed of yellow lupines a crystallisable base has been found of the composition  $C_{10}H_{21}NO_2$ , soluble in water, melting at  $62.5^\circ$ , and boiling at  $269-270^\circ$ . Besides this, two other amorphous alkaloids have been found,  $C_8H_{17}NO$  and  $C_7H_{15}NO$ . None of the three bear any resemblance to coniine. E. W. P.

**Increase of Dry Matter in Several Agricultural Plants during Growth.** (*Bied. Centr.*, 1879, 844—847).—This paper contains a mere statement of the points investigated by various persons. The only research described is that by Messrs. Kreusler, Prehn, and Hornbeyer on maize. It is found that the first great increase of dry matter is attained at the period of maximum development of the male flowers; and that a retrogression of the growth takes place when the seed sets. E. W. P.

**Absorption of Oxygen and Expiration of Carbonic Anhydride by Plants.** By H. MOISSAN (*Bied. Centr.*, 1879, 874).—Every organ of a plant inspires oxygen and gives out carbonic anhydride; expiration of carbonic anhydride is not always accompanied by absorption of oxygen; generally at low temperatures the volume of oxygen absorbed is greater than that of the carbonic anhydride expired; for every species of plant there is a definite temperature at which a given volume of oxygen is replaced by a like volume of carbonic anhydride. E. W. P.

**Constitution of Frozen Beech-leaves.** By J. SCHRÖDER (*Bied. Centr.*, 1879, 875).—The leaves of a beech tree which had been frosted in May appeared to have the same amount of nitrogen and phosphorus as a normal leaf in the same month. E. W. P.

**Composition of Leaves of Diseased Vines.** By E. ROTONDI and A. GALIMBERTI (*Bied. Centr.*, 1879, 876).—Diseased vine leaves contain more moisture than healthy leaves, and in the dry matter there is a higher percentage of nitrogen, ash, phosphoric acid, potash, and soda. E. W. P.

**Dry and Wet Rot in Potatoes.** By J. REINK and G. BERTHOLD (*Bied. Centr.*, 1879, 851—855).—The two classes of rot to which potatoes are subject, namely the dry, in which the tuber becomes loose and spongy, coated on the outside with mould, and the wet, in which the

interior of the tuber becomes partially liquid, the outside being also coated with mould, are not due originally to the fungi *Phytophthora infestans* and *Saprophyte*, but to Bacteria (*Bacillus subtilis* and *Bacterium navicula*). The disease is generally accompanied and aided by the presence of *Phytophthora*, but not always. If a healthy and *Phytophthora*-free potato be inoculated with Bacteria by means of the fluid from a diseased potato, disease will be communicated. Potatoes having a maximum of starch resist the disease most effectually. Potatoes grown on moist soils, and soils containing much organic matter, such as stable manure, are most liable to disease. The starch from diseased potatoes is yellow, but it can be used for the preparation of dextrin of a second quality. E. W. P.

**Comparative Investigation of Hops.** By C. O. HARZ (*Bied. Centr.*, 1879, 848—850).—The proportion in weight of the various parts to one another of several species of hops has been determined, and tables are given of the results. The sp. gr. of the alcoholic extract is about 0.795. The percentage of leaf is about 79, but there appears to be no definite relationship between the lupulin, fruit, or leaves, neither can any be found between lupulin, fruit, and tannin, which last is present to the extent of about 3 per cent. E. W. P.

**Supposed Presence of Catechol in Plants.** By C. PREUSSE (*Bied. Centr.*, 1879, 874).—The author denies the presence of catechol in the leaves of *Ampelopsis hederacea*, and considers that some kind of tannin was mistaken for catechol. E. W. P.

**Influence of Manures on the Combustibility of Tobacco.** By G. CANTONI (*Bied. Centr.*, 1879, 812—814).—The manures employed were, potassium ammonium and calcium sulphates, potassium and sodium nitrates, and potassium and sodium chlorides. The nitrates had most effect as regards vigour of growth, whereas the chlorides and gypsum were prejudicial, the yield in weight being even higher when no manure was applied than when ammonium sulphate or sodium chloride was added. As regarding combustibility, the leaf was almost totally incombustible when the plant had been manured with gypsum, but that produced by potassium sulphate and chloride was completely combustible. E. W. P.

**Combustibility of and Amount of Chlorine in Manured Tobacco.** By A. MAYER (*Bied. Centr.*, 1879, 814—816).—Tobacco manured with chlorides may contain as much as 0.52 per cent. of chlorine, whilst an unmanured plant will only contain about 0.21 per cent. in the leaves of the plant. The author confirms the statement that chlorides have a prejudicial influence on the combustibility of tobacco, as expressed by Cantoni (*vide* preceding paper); it is therefore recommended that no chlorides should be used to manure the tobacco plant, but nitrates in preference. E. W. P.

**Application of Natural Products as Manures.** By F. ULLIK (*Bied. Centr.*, 1879, 801—804).—Some basalts contain a considerable

quantity of potassium and phosphoric acid, but in such a form as not to be easily dissolved by acetic acid, and therefore not readily absorbable by plants; but if the finely ground stone be treated with a 2 per cent. solution of potassium chloride, calcium is eliminated, and the phosphoric acid rendered more soluble. Thus the ratio of the difficultly soluble to the readily soluble potassium in the original basalt is 7 : 1, whereas after treatment the ratio is 4 : 1. In the same way the ratios of the phosphoric acid are 90 : 1 before treatment, and 4·8 : 1 afterwards.

E. W. P.

**Determination of the Chemical Peculiarities of Soils and Manures requisite for them; and on the Action of Soluble and Reduced Phosphates.** By D. v. KÖRN (*Bied. Centr.*, 1879, 805—812).—The soil on which the experiments were performed contained 50 per cent. of clay and sand, and only 0·039 phosphoric acid; the manures were dug in to a depth of 10—12 cm. The special results are naturally only of local interest. Of the three forms in which phosphoric acid is applied, viz., superphosphate, precipitated phosphate, and patent "humus superphosphate" (dried peat saturated with free phosphoric acid), precipitated phosphate seems to have been the most successful.

Another series of experiments was devised to determine the relative value of soluble and reduced phosphates. The results were as follows:—The application of soluble phosphate alone in a calcareous soil has no effect; the application of reduced phosphate has considerable effect; when potash is present, the soluble phosphate still yields the worst results; but when potash and nitrogen were added, the results with barley were equal, except that the straw was increased by the reduced phosphate.

E. W. P.

**Manuring of Sugar-Beet in America.** By C. A. GOESSMANN (*Bied. Centr.*, 1879, 816).—The following are the tabulated results of experiments on sugar-beet:—

| Soil.       | Manure.                            | Sp. gr. of juice of root in deg. Brix. | Percentage of sugar in juice. | Percentage of foreign matter in juice. | Percentage of sugar in soluble matter of juice. |
|-------------|------------------------------------|--|-------------------------------|--|---|
| Sandy loam  | Free stable manure ..              | 16·50                                  | 12·50                         | 4·00                                   | 75·08   |
| Loamy clay  | " "                                | 15·50                                  | 10·05                         | 4·15                                   | 71·80   |
| Alluvial .. | " "                                | 12·75                                  | 9·17                          | 3·58                                   | 71·92   |
| " ..        | Fresh pigs' dung ....              | 13·50                                  | 9·53                          | 3·97                                   | 70·96   |
| Light sand  | None .....                         | 18·50                                  | 13·73                         | 4·77                                   | 74·21   |
| Alluvial .. | Brighton's artificial manure ..... | 14·50                                  | 11·15                         | 3·35                                   | 76·90   |
| Heavy ..    | Stable manure .....                | 12·25                                  | 8·15                          | 4·10                                   | 66·53   |

E. W. P.

**Raising Vines from Seed.** By A. BLANKENHORN (*Bied. Centr.*, 1879, 850).—It is recommended that vines be raised from seed to

avoid the effect of Phylloxera. Attempts to do this have often failed, by reason of the fact that the seed does not ripen until long after the period of ripening of the grape itself. The seeds of a vine which resists the attacks of Phylloxera are stronger in habitus, and more regularly formed.

E. W. P.

## Analytical Chemistry.

**Determination of the Specific Gravity of Liquids.** By H. SOMMERKORN (*Ber.*, 13, 143—144).—The apparatus consists of a tube of thin glass of 3 to 4 cm. diameter, the lower end of which is closed by a thin disc of glass or platinum, having the same circumference as the tube. The disc is held in its position by a thread. The apparatus is immersed in the liquid under examination to such a depth that the pressure is great enough to sustain the disc in its position without the aid of the thread. It is then gradually raised until the point is reached, when the pressure of the liquid is no longer strong enough to support the disc. The length of tube immersed is read off by means of a millimetre scale etched on the glass. The sp. gr. can now be calculated with the aid of the formula  $\frac{G}{a \cdot h} = \text{sp. gr.}$ , where  $G$  represents the weight and  $a$  the area of the disc, and  $h$  the length of tube immersed. Since  $\frac{G}{a}$  is constant, and only  $\frac{1}{h}$  varies with the sp. gr., the specific gravities calculated for the different values of  $h$  may be etched on the tube.

This apparatus yields more correct results than ordinary hydrometers do.

W. C. W.

**New Method of Determining the Fusing Points of Organic Substances.** By G. ROSTER (*Gazzetta*, 10, 13—16).—The author points out that the ordinary method of ascertaining the melting point of a substance as well as Terrell's (this Journal, 1879, Abst., 693), where the substance is attached to the bulb of the thermometer, which is then cautiously heated over a small gas flame, is liable to give inaccurate results. He has, however, modified the last-mentioned process by fixing the thermometer horizontally and placing the substance on the bulb, which is then heated in an air-bath. This air-bath consists of two stout brass tubes, the inner one 3 cm. in diameter and 35 long, closed at one end, and having a small glazed aperture 5 cm. from the open end; the external tube is 8 cm. in diameter and 17 long, and is closed with annular rings at each end, so that it may slide over the internal tube, and is also furnished with a glazed aperture larger than that in the internal tube; when these two windows are brought opposite to one another the interior of the inner tube can be easily seen. To use this apparatus a thermometer with large bulb is fixed horizontally, and a small quantity of the substance whose melting

point is to be determined, is placed on it. The air-bath above described is also fixed on a movable stand at such a height that the axis of the internal tube shall correspond exactly with the thermometer stem; it is then moved forward until the bulb of the thermometer is opposite to the glazed apertures. The extremity of the internal tube remote from the glazed aperture is then heated by means of a gas-lamp, and as soon as any trace of moisture there might be in the interior has escaped, the open extremity of the tube is closed by a loosely-fitting plug which surrounds the stem of the thermometer. The temperature then rises slowly and gradually, and as the substance and the bulb of the thermometer are always at exactly the same temperature the fusing point can be determined with very great accuracy.

C. E. G.

**Estimation of Carbonic Acid in the Air.** By M. KAPUSSTIN (*Ber.*, 12, 2376).—This method depends on the fact that when air containing carbonic anhydride is shaken with a solution of caustic soda in alcohol (90 per cent.) the whole of the sodium carbonate formed is precipitated; sufficient water is then added to redissolve this precipitate, and from the amount of water required, the quantity of carbonic anhydride present is deduced. In an actual experiment, 5 litres of air are shaken for half an hour with 75 c.c. of alcoholic soda (1 litre of this solution = 0.5 gram NaHO), 25 c.c. of the liquid are withdrawn, and water added gradually from a burette until the liquid becomes clear. The amount of carbonic anhydride present in the original volume of air is then found from the equation  $x = \frac{n - 6.5}{0.55}$ , where  $n$  = the c.c. of water required by the whole 75 c.c.

of the soda solution. This method is recommended especially for sanitary purposes, where the number of determinations is of more importance than the great exactness of a single experiment.

T. C.

**Estimation of Aqueous Vapour in the Atmosphere.** By F. RUDBEFF (*Ber.*, 13, 149—152).—In order to determine the amount of moisture in the atmosphere, a three-necked Wolff's flask of 1 litre capacity is used. Each neck is provided with a perforated ground glass stopper; to one of these a manometer containing sulphuric acid (sp. gr. 1.30) is attached. A burette containing strong sulphuric acid passes through the second, and a glass tube provided with a stopcock passes through the third stopper to within a short distance of the bottom of the flask. The first stopper is fitted with a two-way stopcock, so that the flask may be placed either in communication with the manometer or with the external atmosphere.

At the beginning of each determination the stoppers are removed from the perfectly dry flask, and air is blown in to the apparatus from a pair of hand-bellows, the stoppers are replaced, and the manometer placed in communication with the interior of the flask. A small quantity of sulphuric acid is allowed to flow from the burette into the flask, aqueous vapour is absorbed, and the manometer is depressed. After an interval of six minutes sulphuric acid is again slowly added until the manometer regains its normal position. The volume of acid added is equal to the volume of aqueous vapour in the flask.

W. C. W.

**Estimation of Oxygen dissolved in Water.** By J. KONIG (*Ber.*, 13, 154—156).—The author makes the following observations on the paper of Tiemann and Preusse (*Ber.*, 12, 1768, and this vol., 137). The use of Reichard's apparatus (*Zeits. Anal. Chem.*, 11, 271; and this Journal, 26, 412) for expelling the dissolved gases from water in the gasometric method of estimating oxygen yields too high results.

Mohr's process yields slightly too high and Schützenberger's too low numbers. Mohr's method is well adapted for those cases in which an interval elapses between the different analyses, since the strength of the volumetric solutions does not change rapidly. Where a large number of determinations are made in immediate succession, it is advisable to use Schützenberger's process. In this case, it is recommended to ascertain the strength of the sodium hyposulphite solution ( $\text{Na}_2\text{SO}_3$ ) by titration with water saturated with air instead of copper oxide solution.

W. C. W.

**Volumetric Estimation of Arsenic Acid.** By W. A. H. NAYLOR (*Pharm. J. Trans.* [3], 10, 441—443).—Hydriodic acid exerts a reducing action on arsenic acid, and under certain circumstances may be applied to its estimation. The hydriodic acid solution must contain at least 20 per cent. HI, and the iodine estimated as quickly as it is liberated.

To determine the value of an arsenate, a portion equal to 0.05—0.03 gram of arsenic acid is weighed and dissolved in water and a little hydrochloric acid, 5 c.c. of a 20 per cent. hydriodic acid solution are added, and the iodine titrated with sodium hyposulphite. To prevent the oxidation of the hydriodic acid, the operation must be performed in an atmosphere of carbonic anhydride. Towards the end of the reaction, the iodine is liberated at increased intervals, and before taking the final reading 15 minutes should be allowed to elapse. The reaction may be represented by the equation  $\text{H}_3\text{AsO}_4 + 2\text{HI} = \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{I}_2$ . The method may be employed in presence of phosphates and arsenites.

The results given are satisfactory, varying from 2 to .25 per cent. As a qualitative test it may be used to detect 0.0001 gram  $\text{As}_2\text{O}_3$  in 1 gram  $\text{As}_2\text{O}_3$ .

L. T. O'S.

**Valuation of Wine.** By HOUDART and T. PETIT (*Bied. Centr.*, 1879, 858—859).—To assign a value to wine, the following must be determined:—(1) the density  $D$  at  $15^\circ$ ; (2) the amount of alcohol  $a$  present; (3) the weight of the dried extract  $p$  per litre; (4) the mean density  $c$  of this extract. Then let  $P$  = weight of water,  $P_1$  = weight of alcohol contained in 1 litre of wine, whose sp. gr. =  $D$ , and containing  $a$  of alcohol; also let  $d$  = density of water, and  $D_1$  = density of a mixture of pure water and the quantity  $a$  of alcohol: then the weight of a litre of wine will be expressed by the equation  $1,000 D = P + P_1 + p$ . Suppose the extract to be replaced by water, then a mixture will be obtained containing the same amount of alcohol as the wine; let  $D_1$  be the density of such a mixture, and this is found by reference to tables of density. The weight then of a litre of



this mixture is  $1,000 D_1 = P + P_1 + \frac{p}{c}d$ . Subtract the second from the first equation and we have  $1000 (D - D_1) = p - \frac{p}{c}d$ , then

$$c = \frac{pd}{p - 1,000 (D - D_1)}.$$

Another formula may be employed, viz.,

$$p = 2.062 (D - D_1).$$

E. W. P.

**Estimation of the Decolorising Power of Animal Charcoal.** By REINECKE and G. MEYER (*Bied. Centr.*, 1879, 857). The decolorising power of bone charcoal appears to be inversely as its specific gravity.

E. W. P.

**Adulteration and Examination of Food and Drink.** By F. FISCHER (*Dingl. polyt. J.*, 235, 140—150).—*Flour*.—In the Imperial German Act concerning the adulteration of food, &c., flour denotes the grain of corn as prepared in the grinding process. As adulterants the following substances have been used:—

a. Flour of peas, lentils, beans, maize, and potatoes. These are not injurious to health.

b. Gypsum, barytes, chalk, magnesium carbonate, and other mineral constituents, the use of which is injurious.

c. Alum, copper sulphate, and similar metallic salts, which when used in the preparation of bread, are very injurious to health. The colouring of macaronis for soups with picric acid instead of yolk of egg or saffron is also condemned. The methods for analysing flour have been noted elsewhere (*ibid.*, 231; 85, 287).

*Confectionery*.—The following colours are not injurious:—For white: fine meal, starch; red: cochineal, carmine, madder-red, beet-root juice, and cherry-juice; yellow: saffron, safflower, turmeric; blue: indigo, litmus; green: juice of spinach and mixtures of non-injurious yellow and blue colours; for brown: burnt sugar, juice of liquorice; black: Indian ink.

*Meat: sausages*.—Under the following conditions meat is injurious to health:—

1. The meat of animals that have died.
2. The meat of animals afflicted with mania, glanders, splenitis, or with inflammation of the inner organs or outer parts of the body.
3. The meat of animals slaughtered while in a diseased state having shown signs of typhoid appearances or of emaciation.
4. The meat of animals suffering from poisoning, or having been treated with large quantities of poisonous substances previous to being slaughtered.
5. Meat affected with trichinosis or tuberculosis.
6. Meat tainted considerably.

The value of meat is diminished, but without being dangerously injurious:—

1. In all cases of fever and chronic diseases in which consumption has set in.
2. In the case of calves less than eight to ten days old.

3. The nutritive value of sausages is decreased by the addition of flour (*ibid.*, 209, 238).—

4. Horseflesh is often sold as an adulterant for beef (*ibid.*, 203—231).

5. *Milk*.—It would seem that adulteration is of more frequent occurrence with this article than with all other foods or drinks (*ibid.*, 6, 391; 40, 234; 74, 157; 224, 554; 227, 316). The following adulterations are mostly noticed:—

a. Skimmed milk contains less fat than unskimmed milk, and is not suitable for the nourishment of sucklings.

b. Dilution: unskimmed milk and even skimmed milk is often adulterated with water, whereby the nutritive value is lowered.

c. The addition of foreign ingredients to milk (starch, chalk, gypsum, wheat flour, &c.) is not often practised, and is usually made with the view of preventing the detection of the adulteration with water, as they impart to the diluted milk the normal degree of non-transparency and thickness. The author refers to the various methods known for the analysis of milk. He states that milk containing less than 3 per cent., or even 2·8 per cent. fat, or 11·5 per cent. dry substances, should not necessarily be called adulterated.

*Butter*.—According to the German Act, butter is the fat obtained from the milk of mammiferous animals. The increase in weight by adding foreign substances to butter is not allowed. Various other conditions of adulteration of butter are considered in the original, all of which have been published previously. D. B.

**Presence of Sulphuric Acid in Milk.** By G. MUSSO and F. SCHMIDT (*Bied. Centr.*, 1879, 865).—Both authors prove that sulphates are present in milk, although it was formerly stated that they were only present in milk to which spring water had been added. The amount naturally present amounts to 0·0831—0·0391 per cent.

E. W. P.

**Butter Adulteration.** By W. G. CROOKES and others (*Bied. Centr.*, 1879, 861—865).—The processes recommended divide themselves into three classes:—(1) microscopic; (2) specific weight; (3) estimation of the fatty acids.

*Microscopic Test*.—Mylius proposes to examine the butter with a polarising apparatus, in which the Nicol's prism is replaced by one of herapathite. Pure butter which has not been melted shows no signs of polarisation, but if lard, suet, &c., which have been melted, and are therefore crystalline, are present, the crystals appear light on a dark ground.

*Estimation of Specific Gravity*.—König has determined the sp. gr. of several fats at 100°, and finds the sp. gr. of pure butter to be 0·865—0·868; artificial butter 0·859; suet 0·860; mutton suet 0·860; lard 0·861; horse fat 0·861. Mixtures gave intermediate numbers.

*Estimation of Fatty Acids*.—F. Jean saponifies the butter with alcoholic potash, and adds magnesium sulphate after evaporation of the alcohol, washes the precipitate on a filter, and decomposes with hot dilute sulphuric acid. Pure butter should only contain of these solid fatty acids 87—88·2 per cent., whereas oleo-margarin contains

94.1—95.7, and butter of poor quality 90; so that butter having more than 88 per cent. of solid fatty acids may be considered as being adulterated. Reichart saponifies 2.5 grams of butter with 1 gram of solid potash and 20 c.c. 80 per cent. of alcohol and distills the resulting soap with sulphuric acid; the first 50 c.c. of the distillate should require, if the butter be pure, about 14—15 c.c. of decinormal soda solution, but cocoanut fat only 3.7 c.c. and oleo-margarin 0.25—0.95 c.c.; if, then a butter require only 12.5 c.c. of soda it is impure. Koettstorfer's process has already been described (this Journal, Abstr., 1879, 1069).  
E. W. P.

**Testing of Pepsin.** By A. PETIT (*Pharm. J. Trans.* [3], 10, 583—584).—After reviewing the various methods of testing pepsin, namely:—(1) By coagulation; (2) by coagulated white of egg; (3) by filrin, the author concludes that the first method should be rejected, since the principle in rennet which coagulates milk differs from that which dissolves and transforms fibrin.

The second method which is generally adopted has one objection, that it does not establish sufficient gradation in the transformation; it may, however, be used as follows:—An egg is boiled for half an hour, the white passed through a sieve, and 5 grams of the coagulated albumin are treated with 25 grams of hydrochloric acid (1.5 HCl per litre) at 40°. The albumin should be dissolved in four or five hours by 0.10 pepsin. The mixture should be shaken every half hour.

The third method is the most suitable. All the phenomena are distinct and comparable; whatever be the nature of the ferment, all things being equal, its exact equivalence may be determined by reference to other specimens. 5 grams of moist fibrin strongly dried are treated with 25 c.c. of hydrochloric acid (3 grams HCl per litre), and to several flasks thus prepared quantities of pepsin, varying from 0.10 to 0.60 gram, are added and heated to 50°, at which temperature the action of pepsin is a maximum. Agitate every half hour until dissolved, and then every hour: no precipitate should be produced by nitric acid after 6 hours' heating with 0.5—0.6 gram pepsin.  
L. T. O'S.

**Detection of Alizarin, Iso- and Flavo-purpurins; and the Estimation of Alizarin.** By E. SCHUNCK and ROEMER (*Ber.*, 13, 41—43).—These compounds may be separated by fractional sublimation, since alizarin begins to sublime at 110°, flavopurpurin at 160°, and isopurpurin at 170°. The first is easily removed by keeping the temperature below 160°; in the sublimate obtained above 170° the two purpurins may be distinguished by the aid of the microscope, flavopurpurin subliming in fine reddish-yellow needles, whilst isopurpurin sublimes in compact, well-formed rhombic crystals; or they may be separated by means of benzene, in which the latter is insoluble, whilst the former is easily soluble.

The authors propose to apply the above to estimate alizarin. The mixture is heated at 140° as long as a sublimate is obtained and the residue weighed, and thus the alizarin estimated by loss. In applying this method to commercial alizarin, it is necessary first to remove anthraquinone, oxyanthraquinone, anthra-, and isocanthra-flavic acids.

P. P. B.

## Technical Chemistry.

**Action of Sulphuric Acid on Phosphates, especially Calcium Phosphate, in connection with the Manufacture of Superphosphates.** By J. POST (*Ber.*, 13, 57—58).—The author finds that by the use of an acid containing 19·8 per cent.  $H_2SO_4$ , a very complete reaction takes place between it (2 mols.  $H_2SO_4$ ) and calcium phosphate (1 mol.). After a few minutes, the alcoholic extract of the product yields but traces of sulphuric acid.

In various experiments, 54·45, 55·66, 57·1, 58·75, and 61·2 per cent. of phosphoric acid was found, the theoretical being 66·67 per cent.

P. P. B.

**Electro-brass Plating.** By J. J. HESZ (*Dingl. polyt. J.*, 235, 47).—The author uses the following bath, which differs materially from former formulæ:—84 grams sodium bicarbonate, 54 grams ammonium chloride, and 13 grams potassium cyanide are dissolved in 2 litres of water. To render the bath active, the sides of the vessel are covered with a sheet of brass which serve as anode, whilst another piece of brass hangs in the bath and forms the cathode. The current is allowed to pass through the bath for one hour, when it is ready for use. It is better to employ cast brass.

In order to tin directly on zinc, the author uses the following mixture:—50 grams sodium phosphate, 50 grams salammmonic, 25 grams sodium bicarbonate, and 25 grams tin salt dissolved in 1 litre of water. Instead of sodium phosphate, Rochelle salt may be employed.

D. B.

**Composition of Must at different Stages of Ripeness of the Grape.** By E. ROTONDI and A. GALIMBERTI (*Bied. Centr.*, 1879, 877).—As ripening proceeds, the total acid and free tartaric acid diminish, whilst the ash and sugar increase.

E. W. P.

**Patent Process for Preparing Inverted Sugar.** By MAUMENÉ, CAIL, and Co. (*Bied. Centr.*, 1879, 856).—Sugar dissolved in four times its weight of water is boiled with  $\frac{1}{1000}$  concentrated sulphuric acid in silvered or tinned boilers, then neutralised with barium carbonate, filtered, and evaporated. To separate the salts which may be present in solution, alcohol is added, which may be recovered by distillation. By such a process, the crude product obtained in the first stage of the manufacture of sugar may be made available for the making of preserves.

E. W. P.

**Extracts of Narcotic Plants.** By H. BRETET (*Pharm. J. Trans.* [3], 10, 565—566).—To determine the value of various extracts of narcotic plants, extracts were made by the different processes in vogue and the proportion of alkaloid contained in them determined.

Comparative experiments on conium with the extract of the defecated juice and extract by infusion, show that 10 grams of the former yield from 0·01309 to 0·0159 gram conicina, and the latter, 0·01857 to 0·0329 gram.

Analyses of belladonna and datura were made with more uniform results.

1 kilo. of fresh leaves of belladonna:—

|                                 | Grams. | Containing         | Per cent. atropine. | Grams atropine. |
|---------------------------------|--------|--------------------|---------------------|-----------------|
| On clarification of juice yield | 5.16   | coagulum . . . . . | = —                 | = 0.0580        |
| "                               | 29.60  | juice extract ..   | = 0.305             | = 0.1067        |
| Deprived of juice . . . . .     | 15.50  | aqueous extract    | = 0.721             | = 0.1117        |
| When dried . . . . .            | 54.94  | " "                | = 0.721             | = 0.3961        |
| " " . . . . .                   | 48.54  | alcoholic "        | = 1.352             | = 0.6562        |

Alcoholic extract of datura yields 1.442 per cent. alkaloïd.

" " belladonna yields 1.081—1.4 per cent. alkaloïd.

Defecated juice of " " 0.090—0.27 " "

Aqueous extract of datura yields 0.451 per cent. alkaloïd.

" " belladonna yields 0.721—0.180 per cent. alkaloïd.

These results show that the alcoholic extract is much the richest in alkaloïd, the extract by infusion ranks next. The extracts of the non-defecated juice are richer in alkaloïd than the defecated; this confirms the opinion that the extracts of Storck are more active than those of the defecated juice.

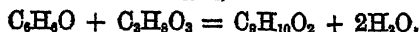
L. T. O'S.

**Manufacture of Resorcinol and Colouring-matters derived from it.** By BINDSCHENLER (*Dingl. polyt. J.*, 234, 484).—An abstract on this subject (*Chem. News*, 38, 226) has already appeared in this Journal (Abst., 1879, 291), but from the article in *Dingler* it would seem that the temperatures formerly given (*loc. cit.*) are in degrees Fahrenheit and not Celsius.

C. E. G.

**New Class of Phenol Colours.** By C. REICHEL (*Dingl. polyt. J.*, 235, 532; from the *Berich. d. Oster. Chem. Ges.*, 1879, 12).—The property which phenol has of giving beautifully coloured compounds with aldehydes, acids, and anhydrides of polybasic acids, induced the author to investigate the action of polyatomic alcohols on the same group of bodies. Similar results were obtained in the case of glycerol, and it appeared, during the investigation, that carbohydrates, mannitol, quercite, erythrol, and ethylene glycol give colours with phenols. The author describes the colours obtained with glycerol and the compounds thymol, cresol, phenol, quinol, orcinol, resorcinol, and pyrogallol, and to these coloured bodies he gives the name of "glycereïnes."

Two parts of phenol, 2 parts of glycerol, and 1 to 2 parts of sulphuric acid heated at 110—120° for a long time, give a dark reddish-yellow resin-like mass; this is well washed and dissolved in alcohol or in soda-lye; the colour is then obtained by diluting the alcoholic solution or by the addition of hydrochloric acid to the soda solution. The substance gave the formula  $C_6H_{10}O_3$ , formed as follows:—



This "phenolglycereïn," a brownish-yellow, amorphous mass, is soluble in acetic acid, alcohol, and in boiling water, but insoluble in benzene and carbon bisulphide. Its solutions acquire a splendid red

colour on the addition of alkalis. With alumina, lead oxide, and other oxides, coloured lakes are produced, and fibrous textures are dyed by it of a violet or yellow tint.

On warming this compound with concentrated sulphuric acid, no sulphur dioxide is evolved, and a sulpho-salt, soluble in cold water, is produced; this solution shades red with alkalis, and is not precipitated with alum.

By heating the mixture of phenol and glycerol with less sulphuric acid, a yellow powder is produced insoluble in ether, benzene, carbon bisulphide, acetic acid, and alkalis: it turns red with the last class of reagents. But its sulpho-compound behaves like that of "phenolglycerein," the sulpho-salt given above.

Five parts of glycerol, 2—5 parts of sulphuric acid, and 6 parts of cresol, heated at 110—120°, yield a dark, glistening, amorphous mass which gives a dark-brown powder. With alkalis it becomes violet-red, and its other properties agree with those of the phenol-colour.

Three parts of thymol, 1 part of glycerol, and 5 parts of sulphuric acid give a corresponding glycerein, similar to the phenol compound as to its solubility, and giving a splendid violet-coloured solution with alkalis. Wool and silk can be dyed violet with this compound.

In a similar manner, 1 mol. each of quinol, glycerol, and sulphuric acid produce the glycerein of quinol. Its alcoholic solution has a beautiful green fluorescence, and becomes brown with alkalis, without losing the fluorescence. In the same way the corresponding compounds of resorcinol and orcinol are obtained. Their alcoholic solutions become red with alkalis, and then show a green fluorescence. On wool and silk they afford pure yellow, reddish- and greenish-yellow colours.

Seven parts of pyrogallol, 5 parts of glycerol, and 2—3 parts of sulphuric acid, heated at 120—130°, give the corresponding compound. The red product contains a new dye which gives a beautiful red shade with tin-salt.

J. T.

**Action of Infusorial Earth on Colouring-matters.** By G. ENGEL (*Dingl. polyt. J.*, 235, 150).—The author thinks that the physical properties of dyeing woven fibres are of much more importance than the chemical. To support this view he has investigated the behaviour of infusorial earth when treated according to the various processes of cotton and wool dyeing, the results of the experiments being noted in *Bull. de Mulhouse* (1879, 659): mordanted and dyed in the same way as wool and cotton, it takes up the dyes quite as well as these substances. Formerly infusorial earth was considered a product of animal origin; but recent investigations have shown that it emanates from the vegetable kingdom. This, however, does not affect its chemical composition.

D. B.

**Mineral Tanning.** By C. HEINZELING (*Dingl. polyt. J.*, 235, 51—53).—The author has patented a process for tanning calf-skin, using (1) alum, (2) zinc-dust, for separating amorphous alumina from the former, (3) chromates, (4) baryta or lead salts, and in case it is necessary to colour the leather black, potassium ferrocyanide. For

the actual tanning process the three first-named substances only are used, the baryta and lead salts being evidently intended only to impart weight to the leather, so that such leather may compete with ordinarily tanned leather. The effective agent appears to be the chromate, but no details of the process are given. Sole-leather cannot be tanned according to this process.

D. B.

**Linaloes-wood.** By J. MOELLER (*Dingl. polyt. J.*, 234, 468—470).—The author has obtained a sample of this wood, the ethereal oil of which is at present largely used in perfumery. The wood is extremely light, porous, almost spongy, has a light yellow colour, with darker, denser, and harder portions, which are quantitatively very subordinate. The wood is without taste. Its aqueous extracts are almost colourless, and do not contain any trace of tannin. The alcoholic extracts also are but slightly coloured, and the author could not succeed in proving the presence of resinous substances with certainty. The examination with the microscope shows, without doubt, that it is only the dense and darker coloured portions of the wood which contain the ethereal oil, whilst the specifically lighter and paler coloured portions—the chief portion in the sample—contain empty cells. The author has not yet been able to collect evidence as to the origin of the wood, and the mode of distillation and preparation of the oil.

D. B.

**Wild Croatian Hops.** By C. O. CECCH (*Bied. Centr.*, 1879, 792).—These cannot be used alone in the preparation of beer, but must be mixed with at least twice their weight of ordinary hops; as they contain large quantities of tannic acid, they may be used with advantage for clearing purposes.

J. K. C.

**Glycerina Cement.** By T. MORAWSKI (*Dingl. polyt. J.*, 235, 213).—Litharge, ground with glycerol, forms a cement which hardens rapidly. The author found, under various conditions, a glyceride of lead in the form of fine needle-shaped crystals of the formula  $C_3H_5PbO_3$ ; but much litharge usually remains uncombined. The combination takes place more rapidly on the water-bath. To prepare the compound quickly, a hot saturated solution of PbO in potash solution is mixed with glycerol, more PbO added to saturation, and the solution quickly filtered: occasionally the compound crystallises out immediately. Heated to  $130^\circ$ , the compound becomes coloured, and at  $200$ — $210^\circ$  it slowly carbonises. Decomposition soon begins on boiling with water, glycerol and lead oxide being separated. It is easily soluble in acetic acid with decomposition, and potash-lye easily dissolves it, especially on warming. It is acted on by nitric and sulphuric acids, although not very rapidly when the acids are concentrated.

The greatest tenacity of the cement is obtained with 50 grams of litharge to 5 c.c. of glycerol.

The author is investigating compounds of glycerol and other metallic oxides.

J. T.

## General and Physical Chemistry.

**Photograph of the Ultra-red Portion of the Solar Spectrum.** By CAPTAIN ABNEY (*Compt. rend.*, 90, 182—183).—The photographs of the portion of the solar spectrum, less refrangible than the A line, were obtained by the use of a silver-compound prepared specially for the purpose, but of which no further details are given.

The wave-lengths are approximately correct; they were obtained by covering half of the slit, and exposing the sensitive surface to the extreme red of a spectrum of the first order, a suitable absorbing medium cutting off the blue end of the spectrum of the second order. The second half of the slit was then opened and the first covered. In this manner the two spectra are superposed, and the wave-lengths were obtained without the possibility of any great error.

This photograph of the prismatic spectrum is in harmony with the thermic observations of Lamansky, and perhaps also with those of Sir J. Herschel. J. W.

**Existence of Carbon in the Coronal Atmosphere of the Sun.** By J. N. LOCKYER (*Proc. Roy. Soc.*, 27, 308).—Photographs have been obtained of the spectrum of carbon, in oxygen and in chlorine, which correspond with the supposed carbon lines in the solar spectrum.

The carbon lines in the solar spectrum are not reversed, showing that the vapour exists at a lower temperature and pressure than the metallic vapours in the sun's atmosphere. It must, therefore, exist above the chromosphere. C. W. W.

**Acceleration of Oxidation caused by the Less Refrangible End of the Spectrum.** By CAPTAIN ABNEY (*Proc. Roy. Soc.*, 27, 291, 451).—The author is of opinion that Becquerel's coloured spectra and Draper's reversed spectra are due to the increased oxidation caused by red rays. Silver bromide, spread on a plate and exposed first to diffused daylight and then to the solar spectrum under a layer of some oxidising solution (hydrogen peroxide, potassium permanganate, nitric acid, &c.), gave a reversed spectrum, extending from D into the ultra-red. No reversal was obtained in an atmosphere free from oxygen.

Silver bromide, which, under ordinary circumstances, is not sensitive below B, when exposed under sodium sulphite, was sensitive to M, the lowest limit (about w. l. 12,000) yet photographed. Silver iodide, under the same conditions, was sensitive to a point between A and  $\alpha$ .

Solarisation is in reality due to the increased oxidation produced by the red rays, and this effect, as is well known, cannot be produced in reducing solutions. It may therefore be concluded that the whole spectrum exercises a reducing action on the sensitive compound, and



that the reduced compound can also be reoxidised, the relative power of these actions appearing to vary with the part of the spectrum employed.

C. W. W.

**Spectra of Metalloids. Spectrum of Oxygen.** By A. SCHUSTER (*Proc. Roy. Soc.*, 27, 383).—Four different spectra of oxygen must be distinguished. At the lowest temperature at which oxygen becomes luminous it gives a continuous spectrum; but as the temperature is gradually raised, the continuous spectrum is successively transformed into two distinct line spectra, which the author names respectively the compound line spectrum and the elementary line spectrum. The fourth spectrum is that which is always seen at the negative pole in vacuum tubes containing oxygen.

The existence of the continuous spectrum is proved by the following facts:—The wide part of a Plücker tube generally shines with a faint yellow light, which gives a continuous spectrum. A weak spark from a coil taken in oxygen at the ordinary pressure gives a continuous spectrum, having its maximum in the greenish-yellow. The point of an oxyhydrogen flame has a yellow colour when excess of oxygen is present (Becquerel); when excess of hydrogen is present, the hydrogen lines are seen (Plücker).

The elementary line spectrum is seen when a strong spark is passed through oxygen at the atmospheric pressure. There are some strong lines which do not appear in Thalén's list. The author has made careful measurements of all the lines.

The compound line spectrum of oxygen consists of four principal lines and a number of fainter ones. The four principal lines, one in the red, two in the green, and one in the blue, are always the first to appear (Wüllner). The following is the appearance of an oxygen tube as it undergoes exhaustion:—When the pressure is sufficiently diminished to allow the spark to pass, it has a yellow colour and gives a continuous spectrum; then the four lines make their appearance, gradually becoming stronger, while the continuous spectrum becomes weaker until at last the lines stand out on a perfectly black background. If now a Leyden jar and air break be introduced, the elementary line spectrum at once comes out. There is a blue line in this spectrum closely, but not exactly, coincident with the blue line in the compound line spectrum; the complete disappearance of the compound line spectrum has, therefore, hitherto escaped notice.

The spectrum of the negative pole consists of fine bands, made up of lines at about equal intervals.

The author considers that the separate spectrum generally seen at the negative pole in gases is due to separate molecular groupings which are formed at that pole. In support of this view, he adduces the fact that when the current is suddenly reversed, the peculiar spectrum is persistent for some time at what was previously the negative pole.

C. W. W.

**Absorption of the Ultra-violet Rays of the Spectra by Organic Substances.** By W. N. HARTLEY and A. K. HUNTINGTON (*Proc. Roy. Soc.*, 28, 233).—The apparatus employed was a combina-

tion of Miller's with Soret's, modified to suit the particular requirements of this research. The object of the research was to trace a connection between the chemical constitution of a body and its actinic absorption. The following conclusions have been drawn:—

(1.) The normal alcohols of the series  $C_nH_{2n+1}.OH$  are remarkable for transparency to the ultra-violet rays, pure methylic alcohol being nearly as much so as water.

(2.) The normal fatty acids exhibit a greater absorption of the more refrangible rays of the ultra-violet spectrum than the normal alcohols containing the same number of carbon-atoms.

(3.) There is an increased absorption of the more refrangible rays corresponding with each increment of  $CH_2$  in the molecule of the alcohols and acids.

(4.) Like the alcohols and acids, the ethereal salts derived from them are highly transparent to the ultra-violet rays, and do not exhibit absorption-bands.

(5.) Benzene and bodies derived from it and its homologues are remarkable firstly, for their powerful absorption of the ultra-violet rays; secondly, for the absorption-bands made visible by dissolving them in water or alcohol and diluting; and thirdly, for the extraordinary intensity of these absorption-bands, that is to say, their power of resisting dilution.

(6.) Isomeric bodies containing the benzene nucleus exhibit widely different spectra, inasmuch as their absorption-bands vary in position and in intensity.

(7.) The photographic absorption spectra can be employed as a means of identifying organic substances, and as a most delicate test of their purity. The curves obtained by co-ordinating the extent of dilution with the position of the rays of the spectrum absorbed by the solution, form a strongly marked and often highly characteristic feature of many organic substances.

C. W. W.

**Thermo-electric Properties of Liquids.** By G. GOBE (*Proc. Roy. Soc.*, 27, 513).—When two plates of the same metal are immersed in a liquid which does not act chemically on them, and one of the plates is heated, an electric current is generated, the direction of which depends on the nature of the liquid. In strongly acid solutions the cold metal is positive to the hot; in strongly alkaline solution the hot metal is positive to the cold. The direction of the current depends on the nature of the liquid; its magnitude is often greatly affected by the kind of metal employed, although no chemical action takes place.

The strength of the current is often greatly increased by maintaining the temperature of the hot plate for some time; in a few cases it was decreased.

The heat applied seems to be the sole cause of the electricity generated.

C. W. W.

**Density of Chlorine at High Temperatures.** By J. M. CRAFTS (*Compt. rend.*, 90, 183—186).—The modification of Meyer's apparatus for the determination of vapour-densities, devised by the author, consists in connecting the porcelain cylinder with two U-tubes, which are

calibrated and divided in tenths of cubic centimeters. One branch of these tubes is connected with a moveable vessel by which the pressure can be controlled, and the other branch terminates in a bulb or reservoir of 9 or 10 c.c. capacity, which communicates by means of a capillary tube with the cylinder. One of the tubes delivers its gas through a narrow tube of platinum or clay to the bottom of the cylinder, while the expelled air passes into the second U-tube to be measured. The tubes are filled with mercury, water, or sulphuric acid, according to circumstances, and are surrounded by cold water to maintain them at an equable temperature.

Two experiments, conducted at the highest temperature of the furnace, showed that 10 c.c. of chlorine occupied the same volume as 10.37 c.c. and 10.24 c.c. of air at the same temperature. There was, however, a small progressive diminution of volume, so that six minutes after the first observation the volume had contracted by 0.04 c.c., and after the second 0.05 c.c. This alteration in volume is probably owing to some action of the chlorine on the tobacco-pipe stem used to convey the gas down the cylinder.

When the apparatus was filled with dry chlorine and heated as before, 10 c.c. of air displaced 9.98 c.c. and 10 c.c. of chlorine. The density of chlorine, according to Meyer, requires in the first series of experiments an expulsion equal to 15 c.c., and in the second to 6.6 c.c. Two other experiments with a thick platinum tube gave 10.43 c.c. and 10.3 c.c. of air displaced by 10 c.c. of chlorine. Bromine, the density of which at 445° was 5.24 (theory 5.57), had at the same temperature as the chlorine, densities of 4.39 and 4.48. Iodine, the density of which at 445° was 8.657 (theory 8.795), gave in a similar manner results which showed that its density was reduced to 6.01 and 5.93. It must therefore be admitted that at the highest temperature of Perrot's furnace iodine diminishes in density to increase in volume in the proportion of 1:1.5, and bromine in the proportion of 1:1.2; in the case of chlorine the increase in volume is 0, or at most only a few hundredths, and therefore nothing like an augmentation of 50 per cent., as originally obtained by Meyer.

J. W.

**Behaviour of Chlorine at High Temperatures.** By V. MEYER and H. ZÜBLIN (*Ber.*, 13, 399—401).—The dissociation of chlorine to molecules of the size  $\frac{1}{2}\text{Cl}_2$ , which occurs (*Ber.*, 12, 1430) in the case of *nascent* chlorine obtained from platinous chloride at or above 1200°, does not take place at similar temperatures if *ready-formed* chlorine be employed; in the case of iodine, however, this dissociation takes place even when the element is used in the free state. These results agree with those of Crafts (preceding abstract).

T. O.

**Density of Bromine at High Temperatures.** By V. MEYER and H. ZÜBLIN (*Ber.* 13, 405—407).—At a temperature of about 1570° the density of bromine in the *nascent state* (evolved from platinic bromide) corresponds to  $\frac{1}{2}\text{Br}_2$ , so that bromine exhibits exactly the same phenomenon of dissociation as nascent chlorine and free iodine under similar conditions.

The density of bromine when employed in the *free state* was very

difficult to determine at the same high temperature, owing to the explosive violence with which the element is converted into gas. The several numbers obtained, however, all lie between those for  $\text{Br}_2$  (5.52) and  $\frac{1}{3}\text{Br}_3$  (3.64), and this agrees with the results of Crafts (this vol., p. 432). T. C.

**Behaviour of Iodine at High Temperatures.** By V. MEYER (*Ber.*, 13, 394—399).—At high temperatures iodine behaves exactly like chlorine. Up to at least  $600^\circ$ , its density corresponds to  $\text{I}_2$ , at  $800^\circ$  it is much less, but remains constant between  $1027^\circ$  and  $1567^\circ$ , when the density corresponds to  $\frac{1}{3}\text{I}_3$ . It differs from chlorine, however, in that the temperature at which the density is diminished by one-third is much lower, being  $1000^\circ$  in the case of iodine, whilst for chlorine it is  $1200^\circ$ . These results agree with those of Crafts (*Compt. rend.*, 90, 184, comp. preceding abstract), but are at variance with those obtained by Deville and Troost (*Ann. Chim. Phys.* [3], 58, 293), according to whom iodine has a normal density at  $1040^\circ$ . T. C.

**Density of Iodine at High Temperatures.** By J. M. CRAFTS and F. MEIER (*Compt. rend.*, 90, 690—692).—According to the well-known experiments of Deville and Troost the density of iodine is normal at  $860^\circ$  and  $1040^\circ$ , whilst, according to V. Meyer, the density of this element is abnormal above  $590^\circ$ . The authors have found that Meyer's method of determining the temperatures by measuring the volume of gas consumed in a given time gives inaccurate results. In their own experiments they have employed the method previously described (this vol., p. 431), the determination of the temperature being made immediately before that of the density. The iodine used was prepared by Stas's method. The numbers obtained are given in the following table as compared with those of V. Meyer. The third column shows the ratio between the experimental and theoretic densities:—

| Crafts and Meier. |          |                | V. Meyer.    |          |                |
|-------------------|----------|----------------|--------------|----------|----------------|
| Temperature.      | Density. | $\frac{D'}{D}$ | Temperature. | Density. | $\frac{D'}{D}$ |
| $445^\circ$       | 8.74     | —              | $450^\circ$  | 8.85     | —              |
| 830—880           | 8.07     | 0.92           | 586          | 8.72     | 0.99           |
| 1020—1050         | 7.01     | 0.80           | 642          | 6.76     | 0.77           |
| 1275              | 5.82     | 0.66           | 1030         | 5.75     | 0.66           |
| 1390              | 5.28     | 0.60           | 1570         | 5.70     | 0.65           |

From the authors' results, it would appear that the density of iodine gradually decreases with a rise of temperature up to  $1400^\circ$ , and is not, as Meyer's figures would show, constant between  $1000^\circ$  and  $1570^\circ$ . Probably at still higher temperatures the density would be reduced to half its normal value, or  $\text{I}_4$  would become  $2\text{I}$ . C. H. B.

**Observations on Vapour-densities.** By V. MEYER (*Ber.*, 13, 401—404).—The author endeavours to account for the conflicting results obtained by himself (see previous abstracts) and by Deville

and Troost (*Ann. Chim. Phys.* [3], 58, 293) in reference to the vapour-density of iodine at high temperatures, by the fact that the conditions of the experiment were very different in the two cases. Deville and Troost placed the iodine in the *cold* apparatus, which was then slowly heated, whereas, in the author's experiments, the element was *thrown directly into the red-hot* vessel, and hence passed almost instantaneously from the solid to the gaseous state. It is therefore not improbable that in this latter case a dissociation would occur which, under other conditions, would not be observed, or only at much higher temperatures. Further, in the author's experiments, the iodine vapour was always in contact with a foreign gas, which was not the case in those of Deville and Troost. Now it is well known that the presence of a foreign, chemically indifferent gas sometimes exercises a very remarkable influence on the molecular condition of the gas; so that the dissociation of complicated molecular groups, which under other circumstances can only be obtained at a high temperature, takes place at a comparatively low temperature if a foreign gas be present, probably owing to the latter diminishing the partial pressure on the vapour in question. This is the case with the vapour of acetic acid, as shown by Horstman (*Ber.*, 3, 78; 11, 1278). This effect appears to be independent of the nature of the indifferent gas.

T. C.

**Vapour-densities of the Alkali-Metals.** By V. MEYER (*Ber.*, 13, 391—394).—The vapour-densities of potassium and sodium cannot be determined in vessels of glass, porcelain, iron, silver, or platinum, as all these substances are attacked by the metals at the temperature necessary for the determinations. The author is now trying vessels of graphite.

T. C.

**Calorimetric Temperature-determinations.** By V. MEYER (*Ber.*, 13, 407—408).—This is a reply to Crafts's remarks (*Compt. rend.*, 90, 184) on the author's method of determining the temperature in his vapour-density investigations. From his own observations, as well as those of Roscoe (*Ber.*, 11, 1196), the author considers that the measurements of temperature given by the calorimeter are accurate enough for the purpose in question, as only an approximate and not an exact knowledge of the temperature is necessary.

T. C.

**Density of some Gases at a High Temperature.** By J. M. CRAFTS (*Compt. rend.*, 90, 309—312).—By means of a modification of V. Meyer's vapour-density apparatus, the author has proved that carbonic anhydride and hydrochloric acid have a normal density even at the highest temperature of a Perrot's furnace (about 1350°). He finds that at very high temperatures porcelain is permeable to hydrogen and aqueous vapour, and suggests that the small quantity of oxygen obtained by Meyer in his experiments on the vapour-density of chlorine may have been due to the action of the chlorine on a small quantity of aqueous vapour which had diffused into the apparatus.

C. H. B.

**Further Remarks on the Heat of Formation of Gaseous Chloral Hydrate.** By BERTHELOT (*Compt. rend.*, 90, 491).—A

continuation of the discussion with M. Wurtz. The author points out that by operating at a low pressure, the mass of matter reacting is so far reduced that the total elevation of temperature cannot be more than one or two-tenths of a degree, a quantity within the limits of experimental error. Moreover, the quantity of matter passing through the apparatus in a given time was probably only small, and the relation between the vapour of water and that of chloral was uncertain. Then, again, everything tends to show that chloral hydrate is partly dissociated at  $100^{\circ}$ , and at a low pressure this dissociation would probably become complete. C. H. B.

**Reply to Berthelot concerning Chloral Hydrate.** By A. WURTZ (*Compt. rend.*, 90, 572).—Since Berthelot admits that chloral hydrate is dissociated at  $100^{\circ}$ , and that the decomposition tends to become complete at this temperature when the pressure is low, it is useless to continue the discussion. The author points out that when operating at ordinary pressures he always noticed a slight decrease in temperature, and that he employed a low pressure in order that the vapours might be dry. The quantity of chloral hydrate formed varied from 20–40 grams in ten minutes. C. H. B.

**Action of Water on Silicon and Boron Fluorides: Solution of Cyanogen in Water.** By H. HAMMERL (*Compt. rend.*, 90, 312–313).—The decomposition of an equivalent (104 grams) of silicon fluoride by water evolves 22.34 cals. The decomposition of an equivalent (68 grams) of boron fluoride evolves 24.51 cals. A molecular volume of cyanogen gas (22.3 liters) develops heat = + 6.8 cals. on solution in water. C. H. B.

**Comparison of the Curves of the Tensions of Saturated Vapours.** By P. DE MONDESIR (*Compt. rend.*, 528–531).—If instead of constructing the curves on the same scale of temperature a convenient scale is chosen for each one, the points of agreement and disagreement become more marked, and classification is rendered much easier. C. H. B.

**Specific Heats of Solutions of Potash and Soda.** By HAMMERL (*Compt. rend.*, 90, 694–695).—The following results were obtained by Berthelot's method:—

| Potash.                                  |           | Soda.                                     |           |
|--|-----------|---|-----------|
| K <sub>2</sub> O per 100 grams solution. | Sp. heat. | Na <sub>2</sub> O per 100 grams solution. | Sp. heat. |
| 32.72                                    | 0.697     | 38.34                                     | 0.816     |
| 25.48                                    | 0.737     | 25.54                                     | 0.852     |
| 17.60                                    | 0.780     | 19.82                                     | 0.869     |
| 14.98                                    | 0.807     | 14.40                                     | 0.886     |
| 11.16                                    | 0.845     | 7.21                                      | 0.924     |
| 9.85                                     | 0.859     | —   | —         |
| 7.78                                     | 0.833     | —   | —         |
| 6.28                                     | 0.900     | —   | —         |

C. H. B.

**Oxidation of Haloïd Salts.** By H. SCHULZE (*J. pr. Chem.* [2], 21, 407—443).—*Action of Oxygen on Haloïd Salts.*—The chlorides of the alkali-metals, and of barium, mercury, and silver, are not altered when heated in a glass tube through which a current of dry oxygen is passing. The chlorides of lithium, strontium, and calcium lose a very small amount of chlorine. The chlorides of magnesium, aluminium, and zinc are partly decomposed. Lead chloride is converted into an oxy-chloride of constant composition. The chlorides of iron, nickel, cobalt, manganese, copper, and chromium are converted into oxides.

The determination of the energy with which oxygen acts on the various chlorides is beset with insuperable difficulties; but some other points brought out by the experiments are worth notice. Silver oxide is converted at the ordinary temperature into chloride by the action of chlorine gas, and calcium oxide when heated in chlorine forms a chloride with incandescence, whilst ferric oxide is only converted with difficulty to the chloride by free chlorine.

The action of oxygen on these chlorides is quite in accordance with the affinities thus shown, for it is known that ferric chloride is easily decomposed by oxygen, calcium chloride very slowly, and silver chloride not at all. When the protochlorides of iron, tin, and barium are heated in air, they suffer partial oxidation together with formation of a higher chloride. Similarly when chlorine acts on such oxides as are capable of a higher state of oxidation, *e.g.*, oxides of lead and antimony, protoxides of iron, manganese, and tin, a higher oxide is formed in addition to a chloride.

The author's results agree with those which Kunheim obtained by the action of water-vapour at high temperatures on various chlorides, only that water-vapour is more energetic in its action than oxygen.

The bromides are much more easily decomposed by oxygen than the chlorides, and the iodides than the bromides.

The fluorides experimented on were those of sodium, calcium, magnesium, iron, and nickel, and the results obtained throughout were negative. Calcium fluoride, however, is partly decomposed if a trace of aqueous vapour is present, even that derived from the burning gas employed in heating the tube being sufficient.

*Action of Nascent Oxygen on the Haloïd Salts.*—Pieces of various chlorides, bromides, and iodides were dropped into melted potassium chlorate, and oxidation took place to a greater or less extent in each case, the iodides being most easily oxidised, and the chlorides with the greatest relative difficulty. The oxidation was least in case of the alkalis, and increased through the groups of calcium, magnesium, &c., but silver and mercury chlorides were unacted on.

*Behaviour of Oxygen to Haloïd Salts in presence of Acid Anhydrides.*—Iodides, which are only slightly acted on by free oxygen (potassium iodide for instance) are decomposed if an acid anhydride is present with formation of a potassium salt, thus  $2\text{KI} + \text{SO}_2 + 2\text{O} = \text{K}_2\text{SO}_4 + \text{I}_2$ .

Bromides are less readily acted on, and chlorides, especially those of the alkali-metals, even less readily than the bromides, although the heating of mixtures of chlorides and acid anhydrides, in presence of air has been proposed as a means of preparing chlorine on the large

scale. Fluorides are decomposed by some acid anhydrides (silicic and boric), but this happens also when free oxygen is not present.

*Behaviour of Acid Anhydrides with Haloid Salts in absence of Oxygen.*—Potassium iodide is oxidised by some anhydrides, whilst a part of the anhydride is itself reduced to a lower state of oxidation; arsenic anhydride, for instance, yields iodine, potassium arsenate, and arsenious acid. Tungstic anhydride when heated with potassium iodide forms a lower oxide of a deep steel-blue colour, the composition of which has not been determined. From molybdic anhydride an oxide of the composition  $\text{Mo}_4\text{O}_{11}$  has been obtained, while silicic, boric, stannic, titanic, and chromic anhydrides are without action when heated alone with potassium iodide.

Chlorides are decomposed by the anhydrides of chromium, arsenic, sulphur, and phosphorus in absence of air, but chromic anhydride under this condition scarcely acts on the chlorides of the alkali metals. When carbonic anhydride is passed over a heated mixture of calcium chloride and tungstic anhydride, a dioxychloride of tungsten is formed: a dioxylbromide is easily obtained by a similar method.

Molybdic anhydride acts on fluorides with formation of molybdic dioxyfluoride,  $\text{MoO}_3\text{F}_2$ , and phosphoric anhydride forms a phosphorus oxyfluoride, which will be described in another paper. G. T. A.

**Chemical Stability of Matter in Sonorous Vibration.** By BERTHELOT (*Compt. rend.*, 90, 487—491).—The author has made experiments to determine the influence of sonorous vibrations on chemical decomposition or combination. Two notes, one corresponding to 100, the other to 7,200 simple vibrations per second, were without effect on ozone, hydrogen arsenide, ethylene in the presence of sulphuric acid, hydrogen peroxide, and persulphuric acid, even after a considerable interval of time, and although decomposition or combination, as the case may be, is in each instance attended with an evolution of heat. It would appear that matter is stable under the influence of sonorous vibrations, but not under the influence of ethereal vibrations, a difference probably due to the much greater rapidity of the latter.

C. H. B.

**Researches on Chemical Equivalence. Part I. Sodium and Potassium Sulphates.** By E. J. MILLS and T. W. WALTON (*Proc. Roy. Soc.*, 28, 268).—The conception of a chemical equivalent employed in this research is that given in *Phil. Mag.* [5], 1, 14, viz., that the chemical equivalent of a body is that weight of it which does the unit of work.

The method employed in the case of the sulphates of sodium and potassium is the effect produced on the rate of formation of ammonia when nascent hydrogen is made to act on potassium nitrate.

The conclusions which the authors draw are:—

(1.) That sodium and potassium sulphates have a well-marked influence on the above reaction.

(2.) That as more sulphate is added the reaction is accelerated.

(3.) That equal weights of sodium and potassium sulphates have, as nearly as possible, the same working effect.

The last conclusion may be otherwise expressed thus:—



. If the equivalent of potassium sulphate be represented by a certain number, then the equivalent of sodium sulphate is represented by the same number.

C. W. W.

**Researches on Chemical Equivalence. Part II. Hydrogen Chloride and Sulphate.** By E. J. MILLS and J. HOGARTH (*Proc. Roy. Soc.*, 28, 270).—The effects of these bodies on the rotatory power of lactic acid were used as the measure of work done.

Varied quantities of solutions of hydrogen chloride (73 grams HCl per liter) and of hydrogen sulphate (196 grams  $\text{H}_2\text{SO}_4$  per liter) were made to act on a solution of 5 grams of lactic acid at  $100^\circ$ , and the change in rotatory power noted after half an hour.

The results obtained show that although  $2\text{HCl}$  may be the "equivalent" of  $\text{H}_2\text{SO}_4$  in weight of saturation (*i.e.*, in the ordinary sense) it certainly is not the equivalent in the dynamical sense. They also render it highly probable that HCl is equal dynamically to  $\text{H}_2\text{SO}_4$ .

C. W. W.

**The Speed of Reactions.** By B. PAWLEWSKI (*Ber.*, 13, 334—335).—Boguski and Kajander (*ibid.*, 10, 34) have shown that when acids (hydrochloric, hydrobromic, and nitric) act on marble, the rate of the reaction is inversely proportional to the molecular weights of the acids. The author concludes from his experiments on the action of hydrochloric and nitric acids on the carbonates of calcium, strontium, and barium, that the rate is not inversely proportional to the molecular weights, but to the atomic weights of the metal in the respective carbonates.

T. C.

**Supersaturated Saline Solutions.** By C. TOMLINSON (*Proc. Roy. Soc.*, 27, 121, 290).—The author has observed that with a southerly or westerly wind, the action of oils on a supersaturated solution of sodium sulphate is to throw down the seven-atom salt, in a powdery form, during damp weather, but in crystals during fine weather. With a northerly or easterly wind, the oil determined the immediate solidification of the solution.

The author attributes these results to the presence or absence of ozone in the air, and cites various experiments adverse to the conclusions of different observers, that they are due to particles of sodium sulphate in the oils employed.

Oil of cajuput, previously inactive, was rendered active by the action of phosphorus in presence of water. Castor-oil and benzene gave the same result.

Various essential oils and other substances, which were powerfully active, were rendered totally inactive by distillation; but the distillates quickly became active when exposed for a short time to the air, or when a few drops of ozonised water were added.

The solution of sodium sulphate did not solidify by itself even when dropped through the open air while a south-east wind was blowing.

Ozone prepared by means of electricity was found to render inactive oils powerfully active in a very short time. On one occasion when there was a large quantity of ozone in the air (wind N.E.) a paraffin

oil was distilled, and the distillate was found to be powerfully active; the same oil distilled during a south-west wind was quite inactive.

Sodium sulphate solution mixed with inactive oil of cajuput was shaken with hydrogen dioxide, but the solution did not solidify.

Inactive cajuput and paraffin oils shaken up with pure oxygen were rendered active, ozone being formed at the same time. Castor-oil did not act in the same way.

Charcoal, heated and cooled out of contact of air, was inactive when first exposed to the air, but became active after a short exposure during a north-east wind. C. W. W.

**Influence of Coal-dust in Colliery Explosions (No. 2).** By W. GALLOWAY (*Proc. Roy. Soc.*, 28, 410).—Colliery explosions often occur in mines, the air of which contains a very small percentage of fire-damp, and in which the character of the coal precludes the probability of any sudden outburst of that gas. These mines are without exception of a dry and dusty character. The explosion is accompanied by the production of large volumes of smoke and soot, and the timbers, &c., of the mine are found after the explosion (in those cases which are not followed by fire) to be covered by a deposit of coked coal-dust, presenting the appearance commonly called "charred."

The author has made a number of experiments on the conditions of explosion in a dusty mine, the air of which contains a small percentage of fire-damp. He finds that a local explosion in such a mine, by mixing the coal-dust with the air, may extend through an indefinite distance, more especially if the air of the mine contains a small quantity of fire-damp (2 per cent. or even less). If the length of a gallery is very great compared with its diameter, the flame is extinguished in a short time.

The most effectual means of preventing these explosions is to keep the floor of the mine continually wet, either with water alone, or with a weak solution of calcium chloride. C. W. W.

**Dry Fog.** By E. FRANKLAND (*Proc. Roy. Soc.*, 28, 238).—It has been frequently noticed that during fogs near large towns the air is not saturated with moisture, the dew point in one instance being as much as 10° C. below the temperature of the air.

Seeing the possible connection between this phenomenon and the fact that the evaporation of water is greatly retarded by its surface being covered with a film of coal-tar, the author made a series of experiments on the comparative rates of evaporation of water, when freely exposed to a current of air, and when covered with a film of coal-tar or of coal-smoke. It was found that the film retarded the evaporation from 92·7 per cent. to 66·6 per cent.

The results of these experiments point out a condition of very common occurrence, competent to produce "dry fog," whilst they also explain the frequency, persistency, and irritating character of the fogs which afflict our large towns. C. W. W.

## Inorganic Chemistry.

**Researches on Nitrous Anhydride and Nitrogen Tetroxide.** By G. LUNGE (*Ding. polyt. J.*, 233, 63—75 and 155—165).—It has not yet been conclusively proved whether or no nitrous anhydride can exist in the gaseous condition, or whether the gas which shows the empirical composition,  $N_2O_3$ , is simply a mixture of nitric oxide and nitrogen tetroxide, and that this mixture combines and forms nitrous anhydride on being condensed to the liquid form by cooling, or on coming in contact with sulphuric acid to form nitrosyl sulphate or with alkalis to form nitrites.

The solving of this problem has been attempted by physical means (by the absorption spectra) by Luck and Moses, but the author has shown (*Reports, German Chemical Society*, 1878, p. 1643) that these results are not satisfactory because of the difficulty of obtaining nitrous acid free from nitrogen tetroxide, and even if this difficulty could be easily removed, any partial dissociation of the vapour would make the distinction by spectrum analysis unreliable.

The author based his line of research on the well ascertained fact that nitric oxide cannot remain as such in presence of oxygen. According to many chemists, nitrogen tetroxide is exclusively produced, whilst others, e.g., Berzelius and Weber, assert that the tri- and tetroxide of nitrogen are always simultaneously formed, the former being produced in proportion as the nitric oxide outweighs the oxygen in the mixture. When, however, there is an excess of oxygen, it is generally believed that nitrogen tetroxide is exclusively or almost exclusively formed.

It is clear, however, that if nitrogen tetroxide is passed into concentrated sulphuric acid, the quantities of nitrosulphuric and nitric acids formed must differ from the quantities of those bodies produced, if nitrogen trioxide or a mixture of nitric oxide and nitrogen tetroxide in the proportions to form the trioxide be treated in a similar manner; and if it be correct that the tetroxide is invariably formed with nitric oxide in presence of an excess of oxygen, then by passing a mixture of nitric oxide with an excess of oxygen through sulphuric acid, and subsequently examining the products so formed in the sulphuric acid, the problem would be solved. This is the process which the author has followed.

A consideration of the composition of the gases which leave the last leaden chamber and enter the Gay-Lussac tower, together with the composition of the resulting sulphuric acid compound, and of the gases which escape from the Gay-Lussac tower, prove almost conclusively not only that the nitrogen compounds have mainly the empirical formula  $N_2O_3$ , but that nitrogen trioxide actually exists as a gas in presence of free oxygen. The conditions in the sulphuric acid chamber are, however, too complicated for the above inference to be taken as demonstrated beyond doubt.

The author prepared liquid nitrous anhydride and rectified it:

2 liters of ordinary air at 17° were then passed through 50 c.c. of this liquid, which on analysis was found to have suffered no change in composition. In other experiments several cubic centimeters of the liquid nitrous anhydride were placed in a U-tube and evaporated by passing through it a rapid stream of dry air, the mixture of air and vapour was then passed through sulphuric acid, sp. gr. 1.84, and the last named analysed. The total nitrogen present in the sulphuric acid was determined as nitric oxide in the nitrometer, and the oxygen, from the amount of potassium permanganate required to oxidise the nitrogen compounds into nitric acid: from these determinations, the composition of the nitrogen compound or compounds which existed in the sulphuric acid was calculated.

A table of the results of experiments is given from which it is shown generally—

First. That nitrogen trioxide is partly decomposed by simple evaporation, yet a complete decomposition is never effected, either by mixing with a very large excess of air or by submitting the mixture to high temperatures: in all cases a very considerable proportion, up to three-fourths of the total nitrogen trioxide, remains unaffected.

Secondly. The greater the excess of air, the greater the amount of trioxide decomposed, but there are exceptions to this rule.

Thirdly. *Cæteris paribus*, temperature appears to have little or no influence in bringing about the decomposition, and the trioxide exists in presence of a large excess of air even at the temperature of 150°.

W. T.

**Action of Hydrogen Peroxide on Silver Oxide and Metallic Silver.** By BERTHELOT (*Compt. rend.*, 90, 572—577).—When hydrogen peroxide acts on silver oxide in any proportion, the volume of the oxygen evolved is exactly equal to the active oxygen in the peroxide, provided the latter be sufficiently dilute to avoid local elevation of temperature. The result is the same whether the hydrogen peroxide acts on the moist silver oxide, or whether the former be mixed with a solution of silver nitrate and an alkaline hydrate added to the mixture. The residue consists of a mixture of metallic silver and a sesquioxide,  $\text{Ag}_2\text{O}_3$ , in the proportion of 1 mol. of the former to 1 mol. of the latter.

*Silver Sesquioxide* when hydrated forms black flakes, which are soluble in dilute acids with evolution of oxygen and formation of ordinary salts of silver. Hydrochloric acid converts it into silver chloride, without evolution of any free chlorine or the production of hydrogen dioxide. It is decomposed by the carbonic anhydride in the air, with formation of silver carbonate. When dried, it slowly loses oxygen and is transformed into the monoxide. The formation of this compound may be represented by the equation:  $3\text{Ag}_2\text{O} + 3\text{H}_2\text{O}_2 = \text{Ag}_4\text{O}_3 + \text{Ag}_2 + 3\text{H}_2\text{O} + \text{O}_2$ . The same substance is probably produced when ozone acts on the monoxide.

The reaction may be explained by supposing that a compound is formed analogous to the double compound of barium and hydrogen peroxides, thus:  $3\text{H}_2\text{O}_2 + 3\text{Ag}_2\text{O} = \text{Ag}_4\text{O}_3.3\text{H}_2\text{O}_2.\text{Ag}_2$ .\* This compound

\* In a subsequent paper the author assigns to this compound the formula  $\text{Ag}_4\text{O}_6.3\text{H}_2\text{O}$ .—C. H. B.

is at once decomposed into free oxygen and hydrated silver sesquioxide. If the hydrogen peroxide is in excess, the sesquioxide again forms the double compound, which is again split up, and so on until the whole of the hydrogen peroxide is decomposed.

The existence of such a double compound is rendered probable by the fact that if an alkali be added drop by drop to a mixture of hydrogen peroxide and silver nitrate solution at a low temperature, a brown precipitate is formed, but no gas evolved. In a short time oxygen is given off and the precipitate turns black.

Whatever the relative proportions of hydrogen peroxide and silver monoxide, the heat evolved is sensibly the same as that developed by the spontaneous decomposition of the former, viz., + 21.6 cals. Since the heat of formation of silver monoxide is + 7.0 cals., it follows that that of the sesquioxide is + 21.0 cals.

When hydrogen peroxide acts upon finely divided metallic silver, a small quantity of the same oxide is formed, and this may be regarded as the active agent which brings about the decomposition of the dioxide. C. H. B.

**Silver Sesquioxide.** By BERTHELOT (*Compt. rend.*, 90, 653—656).—This compound was obtained by the electrolysis of a 10 per cent. solution of silver nitrate, in the form of large, thick, black, lamellar, striated needles, of brilliant metallic lustre. When exposed to the air at ordinary temperatures, it decomposes with evolution of oxygen, and the formation of a black amorphous powder; a little above 100° the decomposition takes place with explosive violence. Prolonged washing with water also brings about decomposition, removing silver nitrate. Analysis of the freshly prepared substance, rapidly dried by means of blotting paper, without pressure, showed that it is really a compound of silver sesquioxide with the nitrate, and has the composition  $4\text{Ag}_2\text{O}_3 \cdot 2\text{AgNO}_3 \cdot \text{H}_2\text{O}$ , or is probably a salt of argento-nitric acid, corresponding to phosphomolybdic acid, thus—



The substance  $\text{Ag}_2\text{O}_3$  or  $\text{Ag}_4\text{O}_6$  is probably identical with the unstable oxide described in the preceding abstract (*Compt. rend.*, 90, 572).

C. H. B.

**Compound of Calcium Iodide with Silver Iodide.** By MAXWELL SIMPSON (*Proc. Roy. Soc.*, 27, 120).—This salt is prepared by saturating a hot concentrated solution of calcium iodide with moist silver iodide, and crystallises on cooling in long white needles having the composition  $\text{CaI}_2 \cdot 2\text{AgI} \cdot 6\text{H}_2\text{O}$ . It is completely decomposed by the addition of even a few drops of water, silver iodide being precipitated; this reaction affords an easy method of analysing the salt. C. W. W.

**Dicalcium Phosphate.** By A. MILLOT (*Bull. Soc. Chim.* [2], 33, 194—198).—Dicalcium phosphate dried at 100° contains  $5\text{H}_2\text{O}$ , which it does not lose below 115°. It is soluble in ammoniacal ammonium citrate, whilst the phosphate containing 1 mol. of water is only sparingly soluble in ammoniacal ammonium citrate. When boiled with water,

dicalcium phosphate is partially decomposed, calcium phosphate goes into solution and tricalcium phosphate is formed. The whole of the dicalcium phosphate can be converted into tricalcium phosphate by decanting the acid solution, and boiling the residue of dicalcium phosphate and tricalcium phosphate with more water, or by neutralising the acid with chalk. By mixing boiling solutions of sodium phosphate, calcium chloride, and acetic acid,  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is formed, and in the cold,  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ .  
L. T. O'S.

**Effect of Heat on Mercury Di-iodide.** By G. F. RODWELL and H. M. ELDER (*Proc. Roy. Soc.*, 28, 284).—Mercuric iodide, as is well known, is capable of existing in two crystalline forms belonging to different systems, and of passing from the one form into the other by change of temperature or by mechanical means. On heating a mass of the crimson amorphous iodide, it turns yellow at  $126^\circ$ , and of a red-brown colour just below the melting point,  $200^\circ$ . The fused substance has the colour of bromine, solidifies at  $200^\circ$  to a red-brown solid, which speedily becomes yellow, and at  $126^\circ$  passes into the crimson octohedral variety, this last change being accompanied by distinct cracking sounds. The change from the red iodide to the yellow is accompanied by an absorption, the reverse change by an evolution of heat.

The coefficients of expansion of mercuric iodide were determined in the manner and with the apparatus employed in the case of silver iodide (*ibid.*, 25, 280). The index of the apparatus showed a regular expansion of a bar of the iodide (red variety) until the temperature of  $126^\circ$  was reached, when the bar began to change from the octohedral to the prismatic condition, and rapid expansion took place without further rise of temperature. When the change was complete, the temperature was again slowly raised, and regular expansion continued under a higher coefficient than before the molecular change, and this continued until the melting point was reached. The expansion in passing from the solid to the liquid state was also determined. The following are the results obtained:—

Coefficient of cubical expansion for  $1^\circ$  from  $0^\circ$  to  $126^\circ$  (the point of change) = 0.0000344706.

At  $126^\circ$ , during the passage from the red to the yellow variety, the body increased in bulk to the extent of 0.00720407.

Coefficient of cubical expansion for  $1^\circ$  from  $126^\circ$  to the melting point ( $200^\circ$ ) = 0.0001002953.

The changes in volume in a mass of liquid mercuric iodide in cooling from  $200^\circ$  to  $0^\circ$  would be as follows:—

|   |             |
|---|-------------|
| Volume at $200^\circ$ of the liquid mass..... | = 1.1191147 |
| " $200^\circ$ of the solid mass .....         | = 1.0190453 |
| " $126^\circ$ (yellow prismatic) ....         | = 1.0115378 |
| " $126^\circ$ (red octohedral) .....          | = 1.0043337 |
| " $0^\circ$ .....                             | = 1.0000000 |

The authors give a curve illustrating these changes.

The specific gravities corresponding to the five marked conditions shown above are as follows:—

|                                 |         |
|---------------------------------|---------|
| Sp. gr. at $0^{\circ}$ .....    | = 6.297 |
| " $126^{\circ}$ (octohedral) .. | = 6.276 |
| " $126^{\circ}$ (prismatic).... | = 6.225 |
| " $200^{\circ}$ (solid) .....   | = 6.179 |
| " $200^{\circ}$ (liquid) .....  | = 5.286 |

Schiff gives the sp. gr. of the octohedral variety as 5.91; Karsten gives 6.2009, and Boullay 6.320. C. W. W.

**Cubic Alum and Chrome Alum.** By A. POLIS (*Ber.*, 13, 360—367).—The necessary conditions for obtaining alum crystallised either in cubes or in octohedrons are described in detail, and also the overgrowth of chrome alum with potash alum. T. C.

**Certain Dichromates.** By K. PREIS and B. RAYMAN (*Ber.*, 13, 340—343).—*Barium dichromate*,  $\text{BaCr}_2\text{O}_7$ , is obtained by dissolving barium chromate in concentrated chromic acid, and drying the crystalline product at  $100^{\circ}$ . It is decomposed by water into chromic acid and ordinary barium chromate. This fact explains the observation of Schulerud (*J. pr. Chem.*, 19, 36) that only barium monochromate is obtained by precipitating barium solutions with potassium dichromate. The mother-liquid from the precipitate of barium dichromate on standing deposits crystals having the composition of the salt,  $\text{BaCr}_2\text{O}_7 + 2\text{H}_2\text{O}$ , obtained by Bahr and Zettnow (*Jahresb.*, 1853, 358; *Pogg. Ann.*, 145, 167).

*Strontium dichromate*,  $\text{SrCr}_2\text{O}_7 + \text{H}_2\text{O}$ , is identical with the salt described by Bahr (*loc. cit.*), and was obtained like the barium salt. It consists of easily soluble dark-red crystals. A salt containing  $3\text{H}_2\text{O}$  was obtained in one experiment in the form of granite-red deliquescent crystals.

The compounds  $\text{PbCr}_2\text{O}_7$  and  $\text{PbCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  are also described.

T. C.

**Decomposition of Potassium Permanganate by Hydrogen Peroxide.** By BERTHELOT (*Compt. rend.*, 90, 656—660).—It is well known that potassium permanganate and hydrogen peroxide in acid solutions mutually decompose one another. Thénard has shown (*Compt. rend.*, 75, 177) that if the two acid solutions be mixed at a low temperature, the liquid is decolorised, but no oxygen is given off; if the temperature rises, oxygen is rapidly evolved. If the hydrogen peroxide be added to the permanganate, the colour is discharged when the proportion of the peroxide and the permanganate is such that they both contain the same amount of active oxygen, and the whole of this oxygen is evolved when the temperature rises. These facts would seem to indicate the formation of a highly oxidised compound, stable at  $-12^{\circ}$ , but decomposed at the ordinary temperature. The colourless character of the compound, and the non-production of any colour during its decomposition, render it improbable that it is a higher oxide of manganese. It cannot be persulphuric acid, for if the permanganate has been added until the solution just ceased to be decolorised, the liquid retains no trace of any oxidising agent, whereas when permanganate is decomposed by persul-

phuric acid the residual liquid always liberates iodine from potassium iodide. Again, it cannot be ozone, for this substance is insoluble in water, and is not present in any considerable quantity in the oxygen evolved. It would appear, then, that the unstable compound is a sesquioxide of hydrogen,  $\text{H}_2\text{O}_3$ , formed according to the equation  $\text{Mn}_2\text{O}_7 + 5\text{H}_2\text{O}_2 = 2\text{MnO} + 5\text{H}_2\text{O}_3$ , and corresponding with  $\text{H}_2\text{S}_3$  and with various metallic oxides.

C. H. B.

**Platinic Bromide.** By V. MEYER and H. ZÜBLIN (*Ber.*, 13, 404—405).—This compound can easily be obtained by heating spongy platinum with bromine and aqueous hydrobromic acid at  $180^\circ$  in sealed tubes. The residue left on evaporation of the filtered liquid is extracted with water so as to separate any platinous bromide, and the clear liquid again evaporated and dried at  $180^\circ$ . Platinic bromide is a black-brown powder, which is not in the least deliquescent. It is readily soluble in water, and still more easily in alcohol and in ether.

T. C.

## Mineralogical Chemistry.

**Examination of the Yellow Incrustation found on the Vesuvian Lava of 1631: Vesbium.** By A. SCACCHI (*Gazzetta*, 10, 21—37).—The fissures in the immense lava torrent of 1631 are often found coated with an extremely thin green crust, with which one of a yellow colour is occasionally associated. In his attempts to ascertain the composition of this crust, the author has observed reactions differing from those of the known elements, and which he attributes to the presence of a new element, *vesbium*, so called from Vesbio, the ancient name for Vesuvius.

As the crust is too thin to separate mechanically, the pieces of lava are treated with very dilute hydrochloric acid, which dissolves off the crust, forming a blue solution, containing abundance of copper, silica, and other constituents of the lava; the acid solution is evaporated to dryness, heated to  $170^\circ$ , and exhausted with water. The residue consists principally of silica and a vesbium compound, together with a finely divided pulverulent matter which can easily be separated by elutriation; after this has been done, the product is treated with hydrochloric acid, filtered from undissolved silica, and again evaporated to dryness and heated to  $170^\circ$ : the small quantity of copper present is removed by repeated washing with hot water, when the purified vesbium compound remains as a dark-green powder, called *vesbine* by the author. This is hygroscopic, and when ignited becomes brown without fusing. It is soluble in acids, yielding a green solution; the addition of potash or ammonia to this solution precipitates a ferric compound of vesbium, partly soluble in excess of the precipitant, forming a yellow solution. When vesbine is fused with an alkaline carbonate or nitrate, it dissolves with effervescence, forming an alka-



line vesbiate soluble in water; on adding an acid to the colourless solution, it acquires a yellow colour similar to that of a chromate; this becomes bluish-green on heating. Alkaline vesbiates give precipitates of various colours with solutions of metallic salts, that with silver being bright red, whilst the zinc salt is greenish. Attempts to obtain potassium vesbiate in the crystalline state were unsuccessful.

On passing hydrogen sulphide through an acid solution of vesbine, a brown precipitate is produced consisting chiefly of sulphur, but containing small quantities of lead and copper sulphides; the filtrate from this is of a bright blue colour, but becomes colourless on adding excess of ammonia, whilst a brown precipitate is thrown down. When a plate of zinc is immersed in the blue solution, the colour is changed to deep brown, so as to appear almost opaque. Even a very large excess of hydrogen sulphide produces no change in the blue solution. All the vesbium compounds, when fused with microcosmic salts, give a yellow bead tinged with brown in the outer flame, and a green bead in the reducing flame.

C. E. G.

**Phosphates and Boro-phosphates of Magnesia and Lime in the Guano Deposit of Mejillones (Lat. 23—24° S.).** By DOMÉTKO (*Compt rend.*, 90, 544—547).—Whereas the guanos found in lat. 12—13° S. retain the nitrogen of their organic matter, those in lat. 23—24° S. contain mere traces of this element, but are largely charged with phosphates. The most important deposit of these phosphatic guanos forms a belt round the mountain Moiro de Mejillones, which is composed of granitic and syenitic rocks traversed by dykes of compact or porphyritic felspars. The deposit is about 50 meters in breadth, and varies in depth. It rests on banks of disintegrated rock, of which there are two well-marked varieties, *tosca*, a loose white sandy substance free from guano and phosphates, and *ripio*, a brown earthy substance mixed with a considerable quantity of guano, and often containing fragments of the neighbouring rocks. The *ripio* also contains concretions of gypsum, phosphates, and borophosphates of lime and magnesia. The great mass of the guano proper is brown, earthy, and consists mainly of calcium phosphate and sulphate, common salt, and organic matter, with traces of magnesium phosphates, alumina, oxide of iron, and nitrates. The phosphates and borophosphates found in the interior of this mass are—

1. *Guano en roche*, a hard, compact, somewhat crystalline substance, of a grey colour, and consisting mainly of tri-calcium phosphate.

2. *Guano cristalizado*, which includes *double phosphate of calcium and magnesium*,  $(\text{CaO}, \text{MgO})_2\text{P}_2\text{O}_5 + 6\text{H}_2\text{O}$ , found in the crevices of the rock or in the interior of cavities in hard masses of guano. The crystals are colourless, more or less transparent, and have a vitreous lustre. Their faces are indistinct, but the dominant form appears to be a rectangular prism. They have the composition  $\text{MgO}$ , 18.53;  $\text{CaO}$ , 5.80;  $\text{P}_2\text{O}_5$ , 40.13. Water and organic matter 36.00 = 100.46. *Magnesium phosphate*,  $\text{Mg}_3\text{P}_2\text{O}_8$ , sometimes fibrous, sometimes in the form of long pyramidal crystals, having a greyish colour and vitreous lustre. The fibrous varieties have a silky lustre. The pure mineral contains  $\text{MgO}$ , 35.11, and  $\text{P}_2\text{O}_5$ , 64.89 per cent.

3. *Borophosphate of magnesium and calcium*, which occurs in the form of spherical and kidney-shaped concretions, seldom more than 6 cm. in diameter. The exterior of these concretions is soft, but the interior is hard and compact. The mineral is amorphous and of a yellowish-white colour. It is soluble in acids, but after strong ignition is not attacked by nitric acid. On analysis it was found to have the composition:—

|   |       |
|---|-------|
| MgO .....   | 24.38 |
| CaO.....  | 0.14  |
| P <sub>2</sub> O <sub>5</sub> .....                                     | 27.60 |
| B <sub>2</sub> O <sub>3</sub> .....                                     | 6.80  |
| Water and organic matter ..   | 38.30 |
| Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> ..... | 2.30  |

99.52 C. H. B.

**Artificial Production of Spinel and Corundum.** By S. MEUNIER (*Compt. rend.*, 90, 701—702).—By the action of steam on aluminium chloride at a red heat in the presence of magnesium, minute crystals are obtained which have the composition and properties of spinel. They consist of colourless and transparent cubes and octohedrons, have no action on polarised light, are extremely hard, and are not attacked by boiling nitric acid. Periclase, and possibly corundum, are formed at the same time. Attempts to obtain gahnite by substituting zinc for magnesium were unsuccessful, probably on account of the low temperature, but the white powder left in the tube consisted mainly of very distinct hexagonal plates, having no effect on polarised light. They contained no zinc, but consisted simply of alumina. Similar crystals can be easily obtained by the action of steam on aluminium chloride heated to redness in a porcelain tube.

C. H. B.

**Martite from Brazil.** By GORCEIX (*Compt. rend.*, 90, 316—318).—The crystals of martite, which are generally octohedral, are found in the talcose rocks of Boa-Vista in the province of Minas Geraes. They have a brilliant lustre, and are sometimes slightly magnetic. Associated with them are found crystals of limonite, hæmatite, and magnetite, having all the forms common to pyrites, from which they have evidently been derived. The interior of one large cubical crystal composed of a mixture of quartz and limonite, contained octohedral crystals of sulphur. The crystals of martite are composed of a mixture of hæmatite and magnetite, and in all probability have also been derived from pyrites.

C. H. B.

**New Silicates of Aluminium and Lithium.** By P. HAUTE-  
FEUILLE (*Compt. rend.*, 90, 541—544).—L. 5SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub>.Li<sub>2</sub>O, may be obtained by heating silica and alumina with lithium vanadate for several hours to a temperature slightly above the fusing point of the latter. If the alumina and the silica be in the proportion of at least 1 mol. of the former to 5 mols. of the latter, the crystals are large and well defined. They have the composition SiO<sub>2</sub>, 69.03; Al<sub>2</sub>O<sub>3</sub>, 23.74;

2 k 2

$\text{Li}_2\text{O}$ , 6.08; loss, 1.15 = 100.00, corresponding with that of oligoclase. They resist the action of acids, scratch glass easily, and have a sp. gr. of 2.40 at  $10^\circ$ . The crystals are transparent, sometimes milky. The general form is an octohedron with a square base, the ratio of the vertical to the lateral axes being about 0.824. They are bi-refractive, and the faces are frequently striated in a direction parallel to the intersection of the faces of the octohedron with those of the prism. Similar crystals are formed when mica is heated with lithium vanadate.

II.  $6\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Li}_2\text{O}$ , may be prepared by heating lithium tungstate or vanadate with alumina and silica in the proportion of 1 mol. of the former to 6 mols. of the latter. The crystals have the composition  $\text{SiO}_2$ , 72.60;  $\text{Al}_2\text{O}_3$ , 22.00;  $\text{Li}_2\text{O}$  (by diff.), 5.40, and stand in the same relation to orthoclase and albite that the preceding compound stands to oligoclase. They have the hardness of orthoclase, and offer the same resistance to the action of reagents; their sp. gr. is 2.41 at  $11^\circ$ . When prepared by means of the vanadate, this compound crystallises in octohedra, the angles of which are identical with those of the preceding compound. When obtained from the tungstate, the usual form is a very obtuse prism, the edges of which are truncated by the faces of the octohedron observed on the crystals obtained from the vanadate.

These two silicates, which have not yet been found in nature, furnish another example of geometric isomorphism similar to that observed in the case of the triclinic feldspars.

The crystals of the first compound differ from those of the second, in that they are bi-refractive, and depolarise polarised light.

The author proposes to class these compounds with amphigene.

C. H. B.

**Artificial Production of a Leucitophyr identical with the Crystalline Lavas of Vesuvius and Somma. Incipient Crystalline Forms of Leucite and Nepheline.** By F. Fouqué and A. M. LEVY (*Compt. rend.*, 90, 698—701).—By fusing for twenty-four hours at a bright red heat, and then for twenty-four hours at a cherry-red heat, a mixture of silica, alumina, potash, soda, magnesia, lime, and oxide of iron, in proportions representing one part of augite, four of labradorite, and eight of leucite, a crystalline mass is obtained, the optical properties of which correspond exactly with those of the natural lavas. The augite is in small green microliths, the labradorite is in large microliths, twinned according to the same law as albite, and the leucite is in large and small trapezohedrons. Octohedral crystals of magnetite and picotite are also present. If the fused mass be allowed to cool slowly after the first twenty-four hours' fusion, the formation of the crystals of leucite can be distinctly observed.

When thin slices of leucite thus obtained are examined under the microscope, arborescent forms, generally at right angles, are observed. With polarised light, the two series of elements of the right angle are differently tinted, and extinction takes place in the direction of the branches of the cross. Less complicated forms are obtained with artificial nepheline.

C. H. B.

**Artificial Production of Felspars containing Barium, Strontium, and Lead.** By F. FOURCÉ and A. M. LEVY (*Compt. rend.*, 90, 620—622).—By heating mixtures of silica, alumina, sodium carbonate, and strontia, baryta, or lead oxide, in the requisite proportions to a temperature just below their fusing points for forty-eight hours, crystalline masses are obtained which correspond in composition to oligoclase, labradorite, and anorthite, but contain baryta, strontia, and lead oxide in the place of lime. These crystals resemble feldspathic microliths in their behaviour with polarised light, and one of the axes of elasticity coincides with the direction of elongation. The anorthite of baryta is probably orthorhombic, the labradorite of lead is decidedly triclinic, but the determination of the crystalline forms of the other compounds could not be made with certainty. The macle of albite, characteristic of triclinic felspars, was not observed on the artificial products. They all scratch glass, and, with the exception of the oligoclases of baryta, strontia, and lead, and the labradorite of strontia, are attacked by acids. Their specific gravities are given in the following table:—

|                   | Strontia. | Baryta. | Lead. |
|-------------------|-----------|---------|-------|
| Oligoclase.....   | 2·619     | 2·906   | 3·196 |
| Labradorite ..... | 2·862     | 3·333   | 3·609 |
| Anorthite .....   | 3·043     | 3·573   | 4·093 |

None of these artificial products corresponds with the natural triclinic barytic felspar recently described by Descloizeaux (*Bull. Soc. Min.*, 1878).

C. H. B.

**Production of Amphigene.** By P. HAUTEFEUILLE (*Compt. rend.*, 90, 313—316).—Very distinct crystals of amphigene were obtained by fusing potassium vanadate and alumina with fragments of strongly ignited silica at a red heat in a platinum crucible for several days. Some of the faces of these crystals showed striæ similar to those observed on twinned crystals of triclinic felspars. Goniometric measurements proved that the faces and angles are strictly comparable with those of the crystals from Mont Somma described by von Rath. The action of the artificial crystals on polarised light showed that, like the natural crystals from Frascati, they are composed of several systems of repeated twins. The oxygen ratios determined by analysis were 1 : 3 : 8. The crystals have a sp. gr. 2·47, that of the natural crystals being 2·48. Like the latter, they are dissolved by sulphuric acid.

C. H. B.

**Formation of Soils by Weathering.** By J. HAZARD (*Landw. Versuchs.-Stat.*, 24, 225—251).—The author has analysed three rocks, weathered portions from them, and the soils to which they have given rise. First a greywacke consisting of an aggregate of quartz-grains and felspar with mica fragments, a little carbon and crystallised silica. Second, a tolerably coarse-grained granite, consisting of quartz felspar plagioclase mainly, and biotite, with fissures charged with iron oxide; a little apatite and iron pyrites also occur. Third, phyllite, a fine-grained schistose rock, consisting mainly of a lamellar mineral of

the mica group; minute quartz needles permeate the mass, and other minerals occur sparingly. The following results were obtained:—

|   | 1.     | 2.    | 3.    | 4.              | 5.     |
|---|--------|-------|-------|-----------------|--------|
| Moisture .....                                | 0.13   | 2.40  | 1.53  | { —<br>2.27     | 2.49   |
| H <sub>2</sub> O combined .....               | 1.30   | 1.23  |       |                 | 2.13   |
| C .....                                       | 0.29   | 2.42  | —     | —               | 4.87   |
| SiO <sub>2</sub> .....                        | 73.95  | 72.32 | 77.42 | 68.39           | 64.06  |
| Al <sub>2</sub> O <sub>3</sub> .....          | 14.30  | 14.37 | 15.39 | { 18.25<br>5.94 | 16.74  |
| Fe <sub>2</sub> O <sub>3</sub> .....          | 3.72   |       |       |                 |        |
| Mn <sub>2</sub> O <sub>3</sub> .....          | 0.22   | 0.12  | 0.12  | 0.14            | —      |
| CaO .....                                     | 0.97   | 1.15  | 1.23  | 4.27            | 1.52   |
| MgO .....                                     | 1.07   | 0.75  | 0.80  | 1.88            | 1.54   |
| K <sub>2</sub> O .....                        | 1.37   | 1.65  | 1.77  | 1.38            | 1.23   |
| Na <sub>2</sub> O .....                       | 2.86   | 1.57  | 1.68  | 3.25            | 1.19   |
|   | 100.18 | 99.58 | 99.94 | 100.77          | 95.77  |
| Loss on ignition, less<br>water and carbon .. | —      | —     | —     | —               | 4.87   |
|   |        |       |       |                 | 100.64 |

|  | 6.     | 7.              | 8.    | 9.    |
|--|--------|-----------------|-------|-------|
| Moisture .....                               | —      | 0.30            | 1.65  | —     |
| H <sub>2</sub> O combined .....              | 2.58   | 29.5            | 3.23  | 3.53  |
| C .....                                      | —      | —               | 3.00  | —     |
| SiO <sub>2</sub> .....                       | 72.87  | 33.54           | 19.14 | 63.58 |
| Al <sub>2</sub> O <sub>3</sub> .....         | 19.04  | { 23.64<br>7.40 | 25.05 | 27.23 |
| Fe <sub>2</sub> O <sub>3</sub> .....         |        |                 |       |       |
| Mn <sub>2</sub> O <sub>3</sub> .....         | —      | 0.18            | 0.13  | 0.14  |
| CaO .....                                    | 1.73   | 0.86            | 1.30  | 1.41  |
| MgO .....                                    | 1.75   | 1.89            | 1.29  | 1.40  |
| K <sub>2</sub> O .....                       | 1.40   | 2.99            | 1.68  | 1.83  |
| Na <sub>2</sub> O .....                      | 1.35   | 1.16            | 0.75  | 0.82  |
| Quartz .....                                 | —      | 25.42           | 39.35 | —     |
| P <sub>2</sub> O <sub>5</sub> .....          | —      | 0.28            | —     | —     |
|  | 100.72 | 100.33          | 96.57 | 99.94 |
| Loss on ignition, less<br>water and carbon . | —      | —               | 3.00  | —     |
|  |        |                 | 99.57 |       |

1. Fresh greywacke from a quarry, the mean of two analyses. 2. Soil above, taken in a fir-wood. Humus calculated from the C found given as 4.03 per cent.: loss on ignition 7.66 per cent. 3. The inorganic constituents of 2, with the water of 1, calculated to 100 approximately. 4. Mean of two analyses of fresh granite. 5. Soil above the granite, estimated to contain 9.74 per cent. of cellulose and humus, with a loss on ignition of 14.36 per cent. 6. The inorganic constituents of 5 with the water of 4 calculated to 100 approxi-

mately. 7, 8, 9, the corresponding results for the phyllite and its soil.

From the analysis we have the following proportions:—

*Greywacke.*

|             | Silica. | Sesquioxides. | Monoxides. |
|-------------|---------|---------------|------------|
| Stone ..... | 11.79   | 2.92          | 1          |
| Soil .....  | 14.13   | 2.84          | 1          |

*Granite.*

|             | Silica. | Sesquioxides. | Monoxides. |
|-------------|---------|---------------|------------|
| Stone ..... | 5.78    | 2.21          | 1          |
| Soil .....  | 11.69   | 2.06          | 1          |

*Phyllite.*

|             | Silica. | Sesquioxides. | Monoxides. |
|-------------|---------|---------------|------------|
| Stone ..... | 8.54    | 4.53          | 1          |
| Soil .....  | 11.64   | 5.02          | 1          |

In all three soils, the silica has increased, whilst the oxides have diminished; possibly the increase of lime in the phyllite soil may be due to additions made to the soil. The separation of silica into free and combined was only successfully made in the case of phyllite, from which it appears that there is less combined silica in the soil than in the stone.

By neglecting quartz in the analyses of phyllite and its soil, and calculating up to 100, we get:—

|  | SiO <sub>2</sub> . | Sesquioxides. | Monoxides. | Humus. | H <sub>2</sub> O. |
|--|--------------------|---------------|------------|--------|-------------------|
| Unweathered silicate in fresh stone .....            | 44.78              | 41.68         | 9.20       | —      | 4.34              |
| Unweathered silicate plus weathered products in soil | 31.78              | 41.83         | 8.33       | 9.96   | 8.10              |
| Unweathered silicate in soil*                        | 31.78              | 29.68         | 6.53       | —      | 3.08              |
| Weathering products in soil                          | —                  | 12.15         | 1.80       | 9.96   | 5.02              |

The bottom line shows base in excess of that required for the silica. This may be combined with humic acid, so that the phyllite soil may have the following composition:—

|                       |             |   |
|-----------------------|-------------|---|
| Quartz .....          | 39.35       |   |
| Silicate undecomposed | 42.74       | (19.14 SiO <sub>2</sub> + 17.81 sesquioxide + 3.93 monoxide + 1.86 H <sub>2</sub> O.) |
| Humic salts .....     | 14.46       | (6.00 humic acid + 7.37 sesquioxide + 1.09 monoxide.)                                 |
| Water .....           | 3.02        | (1.35 of which is moisture.)  |
|                       | <hr/> 99.57 |   |

\* Obtained by taking the same proportions with the silica of the second line as are found in the first line.

*Determination of absorption, soluble bases, moisture, combined water, carbon, humus (calculated), and loss on ignition.*—The material used was well air-dried and freed from root fibres as far as possible. For the absorption of nitrogen, 50 grams were treated with ammonium chloride solution of known strength; after two days the nitrogen left in the solution was determined, and the c.c. absorbed by the material gives the number in the table. The soluble bases were determined by treating with dilute hydrochloric acid, evaporating to dryness, taking up with concentrated hydrochloric acid and water, &c. The water and carbon determinations were made by elementary analysis.

| Granite.                        |       |       |       |      |       |       |       |
|---------------------------------|-------|-------|-------|------|-------|-------|-------|
|                                 | 1.    | 2.    | 3.    | 4.   | 5.    | 6.    | 7.    |
| Absorption .....                | —     | 13    | 30    | 29   | 37    | 40    | 41    |
| Soluble bases .....             | 11·32 | 14·00 | 12·61 | 9·65 | 11·35 | 12·10 | 9·60  |
| Moisture .....                  | —     | 0·68  | 0·83  | 1·62 | 1·73  | 1·87  | 2·49  |
| H <sub>2</sub> O combined ..... | 2·27  | 2·06  | 2·48  | 2·33 | 2·48  | 2·48  | 2·13  |
| C .....                         | —     | —     | —     | 0·86 | 1·15  | 2·70  | 4·87  |
| Humus (calculated) ..           | —     | —     | —     | 1·72 | 2·30  | 5·40  | 9·71  |
| Loss on ignition .....          | 2·27  | 2·74  | 3·36  | 5·67 | 6·51  | 9·75  | 14·36 |

|                                 | Phyllite. |       |       |       | Greywacke. |       |       |       |      |
|---------------------------------|-----------|-------|-------|-------|------------|-------|-------|-------|------|
|                                 | 8.        | 9.    | 10.   | 11.   | 12.        | 13.   | 14.   | 15.   | 16.  |
| Absorption .....                | 2         | 9     | 25    | 36    | 8          | 40    | 47    | 28    | 24   |
| Soluble bases .....             | 8·87      | 12·40 | 14·36 | 13·38 | 6·62       | 12·20 | 19·11 | 6·80  | 8·73 |
| Moisture .....                  | 0·30      | 0·80  | 1·22  | 1·65  | 0·13       | 1·23  | 2·18  | 2·42  | 2·40 |
| H <sub>2</sub> O combined ..... | 2·95      | 4·44  | 3·67  | 3·23  | 1·30       | 3·55  | 3·94  | 2·03  | 1·23 |
| C .....                         | —         | —     | 0·73  | 3·00  | 0·29       | 0·25  | 0·58  | 4·77  | 2·42 |
| Humus (calculated) ..           | —         | —     | 1·46  | 6·00  | —          | —     | 1·16  | 9·55  | 4·03 |
| Loss on ignition .....          | 3·25      | 5·24  | 6·35  | 10·88 | 1·72       | 5·03  | 7·28  | 14·00 | 7·66 |

Nos. 1, 8 and 12 are the fresh rocks; 2 to 6 are rubble, gradually diminishing in size; 9 and 13 are also rubble; 7 is the granite soil before given; 10 subsoil, and 11 upper soil, both above phyllite; 14, subsoil about 0·80 meter deep, 15, the soil above it, both in a fir-wood, and 16, soil from a meadow, all three being over greywacke.

All three soils are fertile ores. The *absorption* of the rocks increases with rate at which they weather; the greywacke soils show a diminishing absorption probably due to the effect of rain, as they were taken from a hill side.

The absorption increases generally with the increase of the soluble bases, but not invariably. By degrees, the silicates of the sesquioxides pass into clay, which absorbs, whilst the monoxides are partly washed out, and the soluble bases are diminished. From this it happens, as in the granite, that the last weathering product with 9·6 per cent. of soluble bases has an absorption of 41.

J. T.

**Examination of Volcanic Dust** which fell January 4th, 1880, at Dominica, and of the Water which accompanied it. By DAUBRÉE (*Compt. rend.*, 90, 624—626).—The powder collected after the rain was fine-grained, and resembled puzzuolana. Microscopic examination revealed the presence of colourless grains of labradorite and sanidine, greenish grains of pyroxene, crystals of gypsum, and very distinct cubic crystals of pyrites from 0.2 to 0.33 mm. diameter. Grains of galena were also present. The sand was impregnated with highly deliquescent salts. Analysis of the powder collected in the dry state gave the following results:—

|                                  | KCl.                | NaCl.               | CaSO <sub>4</sub> . | Organic.   |       |
|----------------------------------|---------------------|---------------------|---------------------|------------|-------|
| Soluble in H <sub>2</sub> O .... | 1.96                | 0.63                | 0.28                | 0.70 =     | 3.57  |
|                                  | FeSO <sub>4</sub> . | CaCO <sub>3</sub> . | MgCO <sub>3</sub> . |            |       |
| Soluble in dilute HCl            | 6.20                | 3.60                | 0.80                | — =        | 9.60  |
|                                  | FeS <sub>2</sub> .  | PbS.                |                     |            |       |
| Soluble in HNO <sub>3</sub> .... | 5.30                | 0.65                | —                   | — =        | 5.95  |
| Insoluble in acids.....          |                     |                     |                     |            | 80.30 |
|                                  |                     |                     |                     | Total..... | 99.42 |

No copper was detected.

The rain received in a rain gauge was charged with about 20 per cent. by weight of a somewhat coarser powder. It held in solution 20 parts per 1000 of the salts found in the dry powder.

The presence of pyrites and galena in the powder is a fact worthy of special notice. The former has probably been recently produced in the volcano by the action of the sulphurous vapours, and resembles in appearance the pyrites found in the fumerolles of Iceland.

C. H. B.

**Sketch of the Origin of the Mineral Waters of Savoy.** By L. LÉVY (*Compt. rend.*, 90, 628—630).—The mineral waters of the Savoy Alps may be arranged in three classes: (1) sulphuretted; (2) saline (chlorides and sulphates); (3) carbonated (alkaline, calcareous, or ferruginous). To the first class belong the springs of Aix, Marlioz, and Challes, in Savoie, and of Bromines, la Caille, and Menthon, in Haute-Savoie. Analyses of the three first give the following results in parts per liter:—

|                            | Aix-les-Bains.  |                       |
|----------------------------|-----------------|-----------------------|
|                            | Sulphur spring. | Alum spring.          |
| Temperature .....          | 43.5°           | 44.6°                 |
| Hydrogen sulphide, free .. | 3.37—4.13 mgrm. | 3.74 mgrm.            |
| Sulphur as thiosulphate .. | 3.84 mgrm.      | 3.60 mgrm.            |
| Total solid matter.....    | 0.4925 gr.      | 0.4443 gr.            |
|                            | Marlioz.        | Challes great spring. |
| Temperature .....          | 11°             | 10.5°                 |
| Sodium sulphhydrate .....  | 0.0285 gr.      | 0.3594 gr.            |
| Total solid matter .....   | 0.6383          | 1.3453                |

In the second class are the waters of Bride, Salins, l'Echaillon, and



Bonneval (Tarentaise) in Savoie, and of Saint Gervais in Haute-Savoie. These contain from 16 (Salins) to 5 (Saint Gervais) grams of solid matter per liter, consisting principally of sodium and magnesium chlorides, and calcium and sodium sulphates. Their temperature varies from 30° to 40°, except in the case of Saint Gervais, where the temperature is 20°.

To the third class belong the springs of Saint Simon, Coise, Farette and la Bauche in Savoie, and of Evian and Amphion in Haute-Savoie. These always contain less than one gram of solid matter per liter, and their temperature is from 10° to 12°. The waters of Evian are alkaline and calcareous, those of la Bauche are highly ferruginous.

The sulphuretted springs are found to the east of the axis of elevation of the Western Alps, which stretches from Grenoble to Sallanches, in a district occupied by jurassic and cretaceous limestones traversed by faults. The waters acquire their sulphuretted character whilst percolating through the limestones, which contain concretions of gypsum and pyrites, and also bituminous organic matter.

The saline springs are found to the west of the same axis in a district occupied by triassic beds which consist of white grits, magnesian limestones, glossy schists, gypsum with common salt, and ferruginous-clayey schists.

The waters of the third class are, comparatively speaking, of surface origin, and are found in the old alluvium or in marshes. They derive their carbonic anhydride mainly from the air, and their iron from oxidised pyrites.

C. H. B.

**Composition of the Waters of Cransac (Aveyron).** By E. WILLM (*Compt. rend.*, 90, 547—548).

|                                   | April 15th, 1879. | July 14th, 1879.   |
|-----------------------------------|-------------------|--------------------|
|                                   | Grams.            | Grams.             |
| Free carbonic anhydride . . . . . | 0.0175            | —                  |
| Magnesium sulphate . . . . .      | 1.7920            | 1.9985             |
| Calcium . . . . .                 | 1.5640            | 1.5623             |
| Aluminium . . . . .               | 0.2800            | 0.1760             |
| Manganese . . . . .               | 0.0158            | 0.0704             |
| Nickel . . . . .                  | 0.0007            | 0.0008             |
| Potassium . . . . .               | 0.2230            | { 0.1446<br>0.0908 |
| Sodium . . . . .                  |                   |                    |
| Lithium . . . . .                 |                   |                    |
| Rubidium . . . . .                | traces            | traces             |
| Zinc . . . . .                    |                   |                    |
| Sodium chloride . . . . .         | 0.0151            | 0.0161             |
| Silica . . . . .                  | 0.0790            | 0.0870             |
| Phosphoric and boric acids . . .  | traces            | traces             |
| Total per liter . .               | 3.9696            | 4.1465             |
| Amount directly determined . .    | 3.9820            | 4.1820             |

The mineral matter of the water of Cransac consists mainly of sulphates, and contains sulphates of manganese and aluminium,

together with small quantities of the sulphates of nickel and zinc. Copper, iron, and arsenic are absent, although the mineral matter is probably derived from iron pyrites undergoing decomposition. The amount of potassium present is considerably greater than that of sodium. The analyses (p. 454) of the principal spring (source Basse Richard) made at different dates seem to indicate that the composition of the water is subject to variation.

The temperature of the water is 12·4° C.

C. H. B.

**Mineral Waters of Bussang (Vosges).** By E. WILLM (*Compt. rend.*, 90, 630—633).

|  | Source<br>Salmade. | Source<br>d'en haut. | Source<br>Marie. |
|--|--------------------|----------------------|------------------|
| Temperature .....  | 12°                | 12·5°                | 11°              |
| Total CO <sub>2</sub> .....  | 2·8719             | 2·1890               | 2·4934           |
| (a.) Portion of residue insoluble in water :—                            |                    |                      |                  |
| SiO <sub>2</sub> .....   | 0·0641             | 0·0634               | 0·0536           |
| Fe <sub>2</sub> O <sub>3</sub> .....                                     | 0·0059             | 0·0024               | 0·0024           |
| Mn <sub>2</sub> O <sub>4</sub> .....                                     | 0·0019             | 0·0019               | 0·0020           |
| Al .....   | 0·0012             | 0·0010               | 0·0011           |
| Ca .....   | 0·1519             | 0·1495               | 0·1880           |
| Mg .....   | 0·0506             | 0·0506               | 0·0540           |
| CO <sub>3</sub> .....  | 0·3589             | 0·3546               | 0·4196           |
| As .....   | 0·00047            | 0·00026              | 0·00043          |
| (b.) Portion of residue soluble in water :—                              |                    |                      |                  |
| CO <sub>3</sub> .....  | 0·3801             | 0·3912               | 0·3081           |
| SO <sub>4</sub> .....  | 0·0904             | 0·0896               | 0·0806           |
| Cl .....   | 0·0507             | 0·0572               | 0·0497           |
| Na .....   | 0·3495             | 0·3580               | 0·2890           |
| K .....  | 0·0346             | 0·0360               | 0·0264           |
| Li .....   | 0·00116            | 0·0013               | 0·0010           |
| P <sub>2</sub> O <sub>5</sub> , B <sub>2</sub> O <sub>3</sub> , and F .. | traces             | traces               | traces           |
| Total .....  | 1·54143            | 1·55696              | 1·47593          |

The "source Marie" rises in the bed of the Moselle.

C. H. B.

**Waters of Bourboule.** By A. RICHE (*J. Pharm. Chim.* [5], 1, 302—306). — The springs of Bourboule, viz., Choussy, Perrière, Sédaiges, La Plage, and Fenestre owe their healing properties to the large quantities of arsenic they contain, viz., 0·0068 gram per liter in Perrière and 0·0064 in Choussy. In the case of Perrière and Sédaiges, the quantity of arsenic does not appear to alter; but in the springs of Choussy and La Plage it is slowly decreasing. Periodic analyses made during the year show that the total mineral matter decreases as it has done since 1867 from 5·886 gram per liter in that year to 4·970 gram per liter in 1879. The quantity of mineral matter in the Choussy and Perrière springs is about the same, as is also the proportion of lithium.

L. T. O'S.

## Organic Chemistry.

**Direct Formation of the Chlorobromides of the Olefines and other Unsaturated Compounds.** By MAXWELL SIMPSON (*Proc. Roy. Soc.*, 27, 118, 424).—*Ethylene chlorobromide*,  $C_2H_4ClBr$ . Chloride of bromine was prepared by passing chlorine into a solution of bromine in aqueous hypochlorous acid; on passing ethylene into this solution, an oily liquid separated, boiling after purification at  $108-110^\circ$ , and giving on analysis numbers agreeing with the above formula.

*Propylene chlorobromide*,  $C_3H_5ClBr$ , is prepared in a similar way, and boils at  $118-120^\circ$ .

*Allyl chlorodibromide*,  $C_3H_5ClBr_2$ , is formed by the action of bromine chloride on allyl bromide at the ordinary temperature. It boils at  $197-199^\circ$ . If the mixture be heated to about  $100^\circ$ , *allyl bromodichloride*,  $C_3H_5Cl_2Br$ , b. p.  $180-187^\circ$ , is produced.

*Ethylidene chloriodide*,  $CH_3CHClI$ , may be prepared either by the action of a weak solution of iodine chloride on ethylidene iodide or of aluminium iodide dissolved in carbon bisulphide on ethylidene iodide, also dissolved in carbon bisulphide. After purification, the product distils at  $117-119^\circ$  without decomposition, and has a density of 2.054 at  $19^\circ$ .

*Ethylidene bromiodide*,  $CH_3CHBrI$ , may be prepared in the same way as the chloriodide, substituting the bromide of iodine for the chloride. It boils at  $142-144^\circ$ , and does not solidify in a freezing mixture.  
C. W. W.

**Preparation of Acetylene.** By JUNGLEISCH (*Compt. rend.*, 90, 364-367, and *J. Pharm. Chim.* [5], 1, 307-310).—This is a description of a special lamp for the preparation of acetylene by the incomplete combustion of coal-gas, the supply of air being limited by virtually burning a jet of air in an atmosphere of coal-gas, so as to avoid any excess of oxygen being carried over into the ammoniacal cuprous solution. A description of the apparatus would be incomplete without the diagrams, which are given in the original paper.

L. T. O'S.

**Action of Bleaching Powder on Propyl, Butyl, and Amyl Alcohols.** By J. REGNAULT and E. HARDY (*J. Pharm.* [4], 30, 405-408).—To determine the part played by the above alcohols in introducing impurities in the preparation of chloroform from ethyl alcohol, they were severally treated with bleaching powder. Isopropyl alcohol (b. p.  $82^\circ$ ), isobutyl alcohol (b. p.  $109^\circ$ ), and amyl alcohol (b. p.  $130-132^\circ$ ), were distilled with bleaching powder; in each case the distillate separated into two layers, the lighter consisting of an alcoholic solution of a chlorine compound and the heavier of water. The upper liquid was again distilled with bleaching powder, when the distillate separated into three layers. The heaviest liquid consisted of a chlorine compound, and the other two of the alcoholic solution of the same and water; they were again treated with bleaching

powder and so on until all the alcohol had been converted into the chlorine compound.

The chlorine compounds in each case have properties similar to those of chloroform, but differ from it and from each other. These results show that the isomeric alcohols have some influence on the purity of chloroform. The authors purpose giving a more detailed account of their research in a future communication. L. T. O'S.

**Action of Bromine on Epichlorhydrin.** By E. GRIMAUX and P. ADAM (*Bull. Soc. Chim.* [2], 33, 257—259).—By treating epichlorhydrin with bromine at  $100^{\circ}$ , the latter is rapidly absorbed and an oily liquid obtained, which decomposes on distillation in a vacuum, but deposits crystals on adding water and cooling at  $0^{\circ}$ . The crystals separate from a heavy oil, and recrystallised from alcohol, consist of chlorotribromacetone,  $C_3H_2ClBr_3O \cdot 4H_2O$  (m. p.  $55^{\circ}$ ). Dried in a current of air, the crystals lose their water of crystallisation, and anhydrous chlorotribromacetone is obtained as a heavy, colourless oil, which attacks the eyes.

The oily liquid which is separated from the crystals consists of chlorobromhydrin,  $CH_2Cl.CH(OH).CH_2Br$  (m. p.  $190-195^{\circ}$ ).

The action of bromine on epichlorhydrin may be expressed thus:—



L. T. O'S.

**Action of Sodium on Epichlorhydrin.** By HANBIOT (*Bull. Soc. Chim.* [2], 32, 552).—By the action of sodium on epichlorhydrin, a yellow insoluble body,  $C_6H_{10}O_2 + 2NaCl$ , is produced, from which the sodium chloride cannot be removed by washing. If, however, the reaction is allowed to take place in the cold, a product is eventually obtained which is soluble in cold water. On heating this solution, the yellow substance is precipitated, but by evaporating the cold solution in a vacuum, the sodium chloride crystallises out alone, and an oily liquid is obtained, having a sweet taste and corresponding with the formula  $C_6H_{10}O_2$ . The author thinks it is the anhydride of a tetratomic alcohol, which he hopes to obtain from it by hydration.

J. M. H. M.

**Constitution of Epichlorhydrin.** By HANBIOT (*Bull. Soc. Chim.* [2], 32, 551—552).—In order to decide by experiment be-

tween the two formulæ for epichlorhydrin,  $CH_2Cl.CH \begin{smallmatrix} CH_2 \\ | \\ O \end{smallmatrix}$  and

$CH_2Cl.C.CH_2(OH)$ , proposed by Reboul and by Berthelot respectively, the author mixed gradually 92 grams epichlorhydrin with 130 grams phosphorus trichloride. A violent reaction occurred, and on cooling the mixture and submitting the product to distillation under reduced pressure, a liquid was obtained (b. p.  $133-140^{\circ}$  at 100 mm.) which proved to be a compound of epichlorhydrin and phosphorus trichloride,  $C_3H_5OCl.PCl_3$ ; it is decomposed by water into epichlorhydrin and phosphorous acid. If Berthelot's formula be correct, the hydroxyl should be replaceable by chlorine, isoallylene dichloride,  $CH_2Cl.C.CH_2Cl$  being formed, but no such body was produced in the reaction.

J. M. H. M.

**Inactive Glucose or Neutral Sugar.** By U. GAYON (*Bull. Soc. Chim.* [2], 33, 253—256).—Horsin-Déon (*ibid.*, 32, 121) shows that inverted and inactive sugar have the same composition, and that in the formation of inverted sugar, inactive sugar is first formed and subsequently converted into inverted sugar by hydration. In answer the author refers to previous notes by himself on the same subject, in which he arrives at the same conclusions as Horsin-Déon, but in different ways. Details of the experiments are given in the paper.

L. T. O'S.

**Inactive and Inverted Sugar.** By P. HORSIN-DÉON (*Bull. Soc. Chim.* [2], 33, 256—257).—In reply to Gayon, the author points out that although their results agree, the difference between their communications is, that Gayon states the fact and the author gives the explanation.

L. T. O'S.

**Method of Producing Acetal.** By R. ENGEL and DE GIRARD (*Compt. rend.*, 692—694).—Acetal may be obtained in considerable quantity by passing a current of non-spontaneously inflammable hydrogen phosphide through a mixture of equal volumes of aldehyde and absolute alcohol, cooled to  $-21^{\circ}$ . A small quantity of ethyl ether is also produced. It is probably not necessary to work at so low a temperature, but the authors promise further details.

C. H. B.

**Researches on Lactin.** By E. J. MILLS and J. HOGARTH (*Proc. Roy. Soc.*, 28, 273).—The permanent specific rotation of lactin (milk-sugar) as determined by Jellet's polarimeter is  $59.17^{\circ}$  (mean of 21 experiments). Berthelot gives  $59.3^{\circ}$ .

If the rotatory power of freshly prepared aqueous solution of lactin be examined at short intervals of time, it is found to gradually decrease. This phenomenon was quantified by a series of determinations made at intervals of two hours, in some cases with addition of sodium or potassium chloride; and it was found that the change could be expressed by the equation  $y = a + bx + cx^2$ , in which  $y$  is the angle of rotation,  $x$  the time in half hours, counting from the first contact of the lactin with water, and  $a$ ,  $b$ , and  $c$  are constants. From the results obtained, the initial specific rotation of lactin is calculated to be  $92.63^{\circ}$ . When the specific rotation  $64.8$  is reached, the law of change must be expressed by a different equation; this fact pointing to the dual nature of lactin mentioned by Fudakowski. Increase of temperature hastens the change. The presence of sodium or potassium chloride increases the amount of lactin in solution, but has no apparent effect on the rate of change.

The study of the action of hydrogen nitrate on lactin is attended by great experimental difficulties, but the authors have succeeded in obtaining results which are expressed in a curve. This curve shows a rise in the rotatory power on first addition of nitric acid (due to galactose P), then it falls below zero (formation of mucic acid, and perhaps of lævo-tartaric acid); then a second rise (dextro-tartaric acid), and finally a fall to zero (oxalic acid).

Water at  $17^{\circ}$  shaken with excess of lactin takes up a quantity corresponding to a solubility of one part lactin in 10.64 parts water, the

quantity gradually increasing until it reaches the limit of 1 part lactin in 3.23 parts water. C. W. W.

**Action of Acetic Chloride on Valeraldehyde.** By MAXWELL SIMPSON (*Proc. Roy. Soc.*, 27, 120).—Equivalent proportions of acetic chloride and valeraldehyde were heated in a sealed tube at 100° for about three hours, and the product distilled. About half the liquid passed over between 115 and 145°; the remainder refused to distil even at 300°. On redistillation, the first portion boiled for the most part at 118–128°. It gave on analysis numbers leading to the formula  $C_5H_{10}O$ ,  $AcCl$ . Its sp. gr. is about 0.937 at 17°. It is gradually decomposed by water with formation of hydrochloric acid, acetic acid, and valeraldehyde. C. W. W.

**Action of Dehydrating Substances on Organic Acids.** By B. VANGEL (*Ber.*, 13, 355–358).—It is well known that many polybasic organic acids, either when heated or when subjected to the action of dehydrating agents, give carbonic anhydride, and frequently also carbonic oxide and water, whilst a residue is left depending on the nature of the acid. A more detailed investigation of these facts has led to the following results, attention being paid merely to the nature of the gas evolved:—

*Monobasic acids* when heated with dehydrating agents (sulphuric acid or syrupy phosphoric acid) are either not decomposed at all, or only with difficulty, in which case they give either carbonic anhydride or carbonic oxide; thus stearic and benzoic acids give neither gas by the action of phosphoric acid, and with sulphuric acid they give carbonic anhydride, but no carbonic oxide. *Dihydric monobasic acids* also give either carbonic anhydride or carbonic oxide; thus salicylic gives carbonic anhydride, whilst lactic acid gives carbonic oxide. *Dibasic acids* give equal volumes of carbonic oxide and anhydride, according to the following equation:— $R''(COOH)_2 = R'' + CO_2 + CO + H_2O$ , as in the case of oxalic and camphoric acids. Dumas and Piria found that tartaric acid by treatment with sulphuric acid gave 3 vols.  $CO$ , 1 vol.  $CO_2$ , and 2 vols.  $SO_2$ , but by the action of phosphoric acid, the author states that it gives equal volumes of carbonic oxide and anhydride. *Tribasic acids* give 2 vols. of carbonic anhydride to 1 vol. of carbonic oxide, thus:  $R'''(COOH)_3 = R'''H + 2CO_2 + CO + H_2O$ . This is the case with citric acid, the same result being obtained whether sulphuric or phosphoric acid be employed as the dehydrating agent. Dumas, however, found that citric acid when heated with sulphuric acid gave pure carbonic oxide. Should the above rules be confirmed by further experiments, the author believes that the determination of the nature of the gas evolved on treatment with dehydrating agents would serve as a very ready method for ascertaining the basicity of organic acids. T. C.

**Action of Carbonic Oxide on Alkaline Hydrates at High Temperatures.** By A. GEUTHER (*Ber.*, 13, 323–324).—A claim to priority of discovery over Merz and Tibirica (this vol. p. 374).

**Synthesis of Formic Acid.** By O. LOEW (*Ber.*, 13, 324—325).—Formic acid, ferrous sulphide, ferrous formate, carbonic anhydride, and trithiomethylene are obtained when carbon bisulphide and water are heated with iron filings in sealed tubes at 100°. This method is recommended for preparing formic acid on the large scale.

T. C.

**Action of Titanium Tetrachloride, Stannic Chloride, and Antimony Pentachloride on Acetic Acid and Acetic Anhydride.** By A. BERTRAND (*Bull. Soc. Chim.* [2], 33, 252—253).—The above chlorides act on acetic acid and acetic anhydride, forming mixed anhydrides, which are probably similar to the silico-acetic anhydride of Friedel and Ladenburg (*Ann. Chim. Phys.* [4], 27, 428).

L. T. O'S.

**Compounds of the Myristic Series.** By F. MASINO (*Gazzetta*, 10, 72—78).—As commercial oil of nutmegs is usually more or less adulterated, it was considered preferable to prepare myristin directly from nutmegs by extracting the powdered seeds with ether, which was found to be a far better solvent than either benzene or light petroleum for this purpose. Obtained in this way, it crystallised in colourless lustrous silky plates (m. p. 55°; Playfair found 31°, probably from his substance containing impurities derived from the commercial oil of nutmegs employed). The myristic acid obtained from this by saponification with potash had the melting point (53—54°) given by Heintz.

**Myristamide**,  $C_{14}H_{27}O.NH_2$ , prepared by boiling myristin with alcoholic ammonia for three or four days, crystallises in lustrous scales (m. p. 102°). It is insoluble in water, but easily soluble in alcohol, ether, and benzene. **Myristamylide**,  $C_{14}H_{27}O.NHPh$ , obtained by long continued heating of aniline myristate, crystallises in long slender silky needles (m. p. 84°), which are very soluble in ether, benzene, and chloroform.

**Myristolic acid.**—Bromine does not act on myristic acid even at 120°, but it is readily attacked by chlorine at 100° if exposed to sunshine, hydrochloric acid copiously evolved, and a chlorinated derivative being formed. This was separated from unaltered myristic acid by crystallisation, and heated with alcoholic potash for eight days at 180°; the product contained myristic acid and an oily body, which gave Pertenkofer's reaction, and solidified at a low temperature (m. p. 12°); it united readily with bromine, forming the tetrabrominated derivative  $C_{14}H_{23}Br_4O_2$ . This is a yellow oily substance, which gradually gives off hydrobromic acid when exposed in a vacuum over solid potash, leaving a residue of the composition  $C_{14}H_{23}Br_2O_2$ , which is reconverted into myristolic acid (m. p. 12°) by nascent hydrogen. The quantity of substance was too small to allow of the myristolic acid,  $C_{14}H_{23}O_2$ , to be purified for analysis.

C. E. G.

**Products of the Oxidation of Wool: Cyanopropionic Acid.** By J. A. WANKLYN and W. J. COOPER (*Phil. Mag.* [5], 7, 356).—When wool, dissolved in water by means of three times its weight of potash, is oxidised by four times its weight of potassium permanganate,

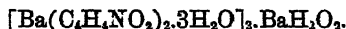
there are produced carbonic acid, oxalic acid, and ammonia; when only two parts of permanganate are employed at least two new acids are produced, one of which, cyanopropionic acid, has been obtained pure.

The free acid, obtained by decomposing the barium salt with sulphuric acid, has the formula  $2C_4H_7NO_2 \cdot 3H_2O$ . It is an amorphous solid, brittle at ordinary temperatures, but softening at  $100^\circ$ . In mass, it has a pale brownish-yellow or straw colour, in powder, it is almost white. It is very soluble in water and in strong alcohol. It has a strongly acid taste and reaction, decomposes carbonates, and dissolves magnesium in the cold. It is oxidised by potassium dichromate and by permanganate.

Heated to  $140^\circ$ , it gives off all its water; at higher temperatures, it is decomposed, evolving ethyl cyanide, and forming a brown mass, soluble in potash.

Most of the metallic cyanopropionates are soluble in water, and contain water of crystallisation.

*Barium cyanopropionate*,  $Ba(C_4H_7NO_2)_2 \cdot 3H_2O$ , is a white powder, very soluble in water, but sparingly soluble in alcohol. It loses 1 mol. of water at  $160$ — $170^\circ$ . There is also a basic salt,



*Silver cyanopropionate*,  $2C_4H_7AgNO_2 \cdot \frac{1}{2}H_2O$ , is nearly insoluble in water; the dry salt quickly absorbs 2 per cent. of water. There is a basic salt,  $2C_4H_7AgNO_2 \cdot AgHO \cdot H_2O$ , obtained by adding silver nitrate to the basic barium salt.

*Lead cyanopropionate*,  $Pb(C_4H_7NO_2)_2 \cdot H_2O$ , is also nearly insoluble in water; it is a white powder.

The *magnesium salt*,  $Mg(C_4H_7NO_2)_2 \cdot 3H_2O$ , is extremely soluble in water, drying up first to a jelly, and finally to a brittle mass, yielding a white powder.

*Potassium cyanopropionate*,  $C_4H_7NKO_2 \cdot H_2O$ , forms a straw-coloured transparent solid. Dried at  $100^\circ$ , the salt contains five molecules of water; at  $190^\circ$ , it contains only one; deposited from strong alcohol and dried at  $100^\circ$ , it contains  $4H_2O$ . It is very soluble in water and in 40 per cent. alcohol, sparingly so in strong alcohol. Heated at  $200$ — $220^\circ$  with twice its weight of potash, it is completely decomposed, giving off ethylamine and leaving potassium oxalate,  $C_4H_7NO_2 + 2KHO = K_2C_2O_4 + C_4H_7NH_2$ , proving the acid to be isocyanopropionic acid.

*Calcium cyanopropionate*,  $Ca(C_4H_7NO_2)_2 \cdot 4H_2O$  (dried at  $100^\circ$ ), is very soluble in water, and is precipitated from its aqueous solution in 84 per cent. alcohol. It loses about 4 per cent. (half a molecule) of water at  $200^\circ$ .  
C. W. W.

**Amides and Anilides of  $\beta$ -Hydroxybutyric Acid.** By L. BALBIANO (*Ber.*, 13, 312—314).— *$\beta$ -Amidobutyramide*,



is obtained by heating ethyl  $\beta$ -chlorbutyrate with alcoholic ammonia in sealed tubes at  $70$ — $80^\circ$ . It is a syrupy liquid, which is easily



soluble in water and in hot alcohol, but only sparingly soluble in ether. Its platinochloride crystallises in orange-coloured tables, which are but little soluble in alcohol, and insoluble in ether. The aqueous solution of the free base evolves ammonia when boiled, and on boiling with lead hydroxide, it gives lead 3-amidobutyrate, from which the free acid may be obtained by treatment with sulphuretted hydrogen. It crystallises in deliquescent plates. The hydrochloride of  $\beta$ -amidobutyramide may be obtained by decomposing the platinochloride with ammonium chloride; it forms a crystalline hygroscopic mass.

On heating ethyl  $\beta$ -chlorbutyrate for several hours with 3 to 4 mols. of aniline a crystalline mass is obtained, which is only partially soluble in ether. The insoluble portion consists of aniline hydrochloride, and the hydrochloride of  $\beta$ -amidobutyranilide,



the latter of which crystallises in brilliant, colourless fatty plates (m. p. =  $206^\circ$ ), which are insoluble in ether, and but sparingly soluble in boiling water.

The portion of the above product which was soluble in ether consisted of unchanged ethyl chlorbutyrate and aniline, together with  $\beta$ -butyranylbetaine,  $\text{C}_{10}\text{H}_{13}\text{NO}_2$ , which was purified by means of its oxalate. It is a crystalline neutral mass, and forms a hydrochloride and platinochloride,  $\text{PtCl}_4 \cdot (\text{C}_{10}\text{H}_{13}\text{NO}_2\text{HCl})_2$ . The free base on boiling with barium hydrate gives barium acetate and resinous products. The oxalate,  $\text{C}_{10}\text{H}_{13}\text{NO}_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ , crystallises in nodules (m. p.  $138^\circ$ ), which are easily soluble in hot water and in hot alcohol, and shows a strong acid reaction. On treating the oxalate with barium hydrate it gives, in addition to the free base, the crystalline barium salt of  $\beta$ -anilobutyric aril,  $\text{NHPh.CHMe.CH}_2\text{COOH}$ , isomeric with the above base. It crystallises in needles (m. p.  $128^\circ$ ), which are but sparingly soluble in cold, but more soluble in hot water; it is easily soluble in alcohol and in ether.

T. C.

**Electrolysis of Malonic Acid.** By E. BOURGOIN (*Compt. rend.*, 90, 608—611).—When an alkaline solution of sodium malonate is electrolysed, the gas evolved at the positive pole consists simply of a mixture of oxygen, carbonic anhydride, and carbonic oxide without any hydrocarbon, whatever the degree of alkalinity or concentration of the solution. With a neutral solution of the salt, carbonic anhydride alone is evolved and the liquid becomes strongly acid in the positive part of the cell. After a time, the carbonic anhydride is accompanied by carbonic oxide and oxygen. With free malonic acid, the gas consists mainly of oxygen with small quantities of carbonic anhydride. Malonic acid, then, differs from succinic acid in that no hydrocarbon is produced when it is electrolysed, and it differs from oxalic acid in its greater stability and in that it concentrates itself in the positive part of the cell.

C. H. B.

**Inactive Malic Acid.** By G. J. W. BREWER (*Ber.*, 13, 351—353).—The inactive malic acid obtained by the author (*ibid.*, 8, 1594) by the reduction of tartaric acid with hydriodic acid consists of a mixture

of dextro- and lævo-rotary malic acids. The two are best separated by means of their cinchonine salts, that of the former being the least soluble in water. The specific rotations of the two acids are  $+6.316$  and  $-2.596$  respectively. T. C.

**Succinin.** By A. FUNARO and L. DANESI (*Gazzetta*, 10, 58—60).—When equal parts of succinic acid and glycerol are heated at  $200^{\circ}$ , a product is obtained which may be purified by dissolving it in water and adding animal charcoal; on cooling, the clear solution becomes turbid and gradually deposits the succinin as an amorphous butyraceous mass of pale-yellow colour. It may be obtained almost colourless by a second treatment with animal charcoal. Succinin,  $C_7H_{10}O_8$ , forms an opaque mass resembling wax in appearance, insoluble in water or alcohol when cold, but easily soluble in the boiling liquid, insoluble in ether, benzene, and chloroform. It is saponified by the action of alkalis in the same manner as other ethereal salts, yielding glycerol and succinic acid. C. E. G.

**Synthesis of Ethylbenzene from Ether and Benzene.** By M. BALSOHN (*Bull. Soc. Chim.* [2], 32, 617—618).—The author has previously shown that in presence of aluminium chloride, ethylene unites directly with benzene, forming ethylbenzene, diethylbenzene, and triethylbenzene. He now shows that ethylbenzene is produced by heating together in sealed tubes at  $180^{\circ}$  for 12 hours a mixture of 1 part ether, 2 parts zinc chloride, and 4 parts benzene. A small quantity of a crystallisable substance is produced at the same time, together with ethylene, and hydrocarbons boiling at higher temperatures than ethylbenzene. J. M. H. M.

**Action of Iodine on Aromatic Compounds with Long Side-chains.** By B. RAYMAN and K. PREIS (*Ber.*, 13, 344—347).—On treating cymene with iodine at high temperatures, it gives the same hydrocarbons as turpentine oil under similar conditions (*Ber.*, 12, 219; this Journal, 1879, Trans., 623), viz., hydrides of toluene and xylene, meta- and para-xylene, mesitylene, pseudocumene, cymene hydride, propyldimethylbenzene, and a high boiling hydrocarbon which gives benzoylbenzoic acid on oxidation.

Amylbenzene and camphor by a similar treatment give in general the same products as cymene and turpentine oil. T. C.

**Fittica's Fourth Nitrophenol.** By S. NATANSON (*Ber.*, 13, 415—417).—The author is unable to confirm Fittica's statement (*ibid.*, 12, 2183) as to the existence of a fourth nitrophenol, for he has several times repeated Fittica's experiments and has only been able to obtain ordinary orthonitrophenol (m. p.  $45^{\circ}$ ), mixed with a little of the corresponding para-compound (m. p.  $114^{\circ}$ ). T. C.

**Ethyl-derivatives of Orthamidophenetol and Orthamidophenol.** By M. FÖSTER (*J. pr. Chem.* [2], 21, 341—375).—Orthamidophenetol is prepared by reducing the nitrophenetol with tin and hydrochloric acid, and after adding soda distilling off the base in a current of steam. Orthamidophenetol is a colourless, oily liquid,

which becomes brown on exposure to the air; it has an aromatic odour and a burning taste, and boils at  $229^{\circ}$  (bar. 756 mm.). It does not solidify at  $-21^{\circ}$ .

*Monethylorthamidophenetol*,  $C_8H_9(OEt).NH.Et$ , is obtained by heating amidophenetol and ethyl bromide in closed vessels at  $60^{\circ}$  for four or five hours; the free base is liberated from the salts so obtained by means of sodium carbonate. It is a colourless, highly-refractive liquid, and boils at  $234-235^{\circ}$  (bar. 751 mm.); its sp. gr. is 1.021 at  $18.3^{\circ}$ . Water and alcohol dissolve it but sparingly; with other ordinary solvents, it mixes in all proportions. It is volatilised by steam. The base becomes brown on exposure to the air, a change also produced by various oxidising agents. With bleaching powder and chloroform the base undergoes a change similar to that observed by Schmitt (*J. pr. Chem.* [2], 18, 196) in the case of aniline; the chloroform solution on evaporation yields a crystalline residue, which is probably an azo-compound. Acetic chloride reacts on the base. This base forms well-crystallised salts, which are easily soluble in water and in alcohol, but insoluble in a mixture of alcohol and ether.

Its *hydrobromide*,  $C_{10}H_{15}NO.HBr$ , crystallises in beautiful colourless rhombic tables, which redden on exposure to air.

The *hydriodide*,  $C_{10}H_{15}NO.HI$ , forms yellowish rhombic leaflets.

The *hydrochloride*,  $C_{10}H_{15}NO.HCl$ , forms long colourless prisms. Its solutions, when treated with platinum chloride and concentrated hydrochloric acid, give a *platinochloride*,  $(C_{10}H_{15}NO.HCl)_2PtCl_4$ , in long, yellow, opaque, rhombic prisms or tablets. It is easily soluble in water; the aqueous solutions are decomposed on boiling; alcohol dissolves it easily, but it is insoluble in a mixture of alcohol and ether.

The oxalate obtained by mixing alcoholic solutions of the acid and base crystallises in colourless, short, thick prisms, which are easily soluble in water.

The sulphate crystallises in small rhombic plates, and the nitrate in long colourless rhombic columns.

*Monethylnitro-orthamidonitrosophenetol*,  $C_8H_9(NO_2)(OEt).N(NO)Et$ , is obtained by the action of nitrous acid on an alcoholic solution of ethylorthamidophenetol hydrochloride; it is insoluble in water, slightly soluble in alcohol, from which it crystallises in yellowish prisms. It is not acted on by acids or alkalis. The nitro-group in this body is reduced by tin and hydrochloric acid, forming a base which is easily attacked by the air.

*Monethylorthamidophenol*,  $C_8H_9(OH).NH.Et$ , is prepared by heating the phenetol with concentrated hydrochloric acid in sealed tubes at  $130^{\circ}$ . The free base, prepared by treating the hydrochloride so obtained with caustic soda, crystallises from ether or benzene in small white rhombic plates, which become brown on exposure to the air; it melts at  $167.5^{\circ}$ , and is decomposed by distillation. It is only sparingly soluble in chloroform, but easily in alcohol. Bromine reacts with the base, forming brown resinous products; a similar change is produced by potassium dichromate and sulphuric acid. Bromine-water and bleaching powder produce a violet, changing to a brown coloration.

*Monethylorthamidophenol* is a weak base, its salts crystallise well, but appear to be decomposed by the evaporation of their aqueous solu-

tions; they are prepared by adding acids to the alcoholic solution of the base and allowing it to evaporate slowly. The salts are easily soluble in water and alcohol, but only sparingly in concentrated acids; they become brown on exposure to air.

The *hydrochloride*,  $C_6H_{11}NO.HCl$ , crystallises in colourless needles or acute rhombic prisms, and may be sublimed by heating carefully.

The *platinochloride*,  $(C_6H_{11}NO.HCl)_2PtCl_4$ , crystallises in long yellowish needles united in rosette-like groups. It is easily soluble in water and alcohol, and is decomposed on boiling with separation of platinum.

The *hydrobromide*,  $C_6H_{11}NO.HBr$ , forms small colourless prisms, which, when carefully heated, may be sublimed.

The *hydroiodide* crystallises in yellow acuminate needles; it is very unstable. The oxalate resembles that of the phenol.

*Orthamidonitrosophenol*,  $C_6H_4(OH).N(NO)Et$ , is obtained by the action of nitrous acid on the alcoholic solution of orthamidophenol hydrochloride; it is precipitated from its alcoholic solutions by water in greyish leaflets (m. p.  $121.5^\circ$ ). It is insoluble in water, but soluble in other ordinary solvents, and is not acted on by alkalis or acids. Tin and hydrochloric acid convert it into amidophenol.

*Diethylorthamidophenetol*,  $C_6H_4(OEt).NEt_2$ , obtained by heating an alcoholic solution of orthamidophenetol and ethyl iodide in sealed tubes at  $120-130^\circ$ , and decomposing the iodides so obtained with sodium carbonate. The free base is a colourless oily liquid, boiling at  $227-228^\circ$  (bar.  $754.3$  mm.), and having an aromatic odour. It is insoluble in water, but soluble in other ordinary solvents. On exposure to air, it becomes yellow; bleaching powder gives a reddish-violet coloration, changing to a red; and bromine-water and other oxidising agents produce a red solution. It is not acted on by acetic chloride. Concentrated sulphuric acid dissolves it, forming a violet solution, which becomes yellow when diluted. Its salts form thick gelatinous masses.

*Diethylorthamidophenol*,  $C_6H_4(OH).NEt_2$ , is obtained from the phenetol by the action of concentrated hydrochloric acid. It is a colourless liquid of aromatic odour boiling at  $218-220^\circ$ , and becomes green on exposure to air; the green solution when heated becomes yellow, and on cooling assumes the green colour. It is insoluble in water, but soluble in alcohol, ether, &c. Oxidising agents produce a reddish-brown coloration in its solutions. Bleaching powder gives a red-coloured solution from which a dark resinous body separates. Bromine water gives a yellow cloudiness, then a blackish-brown resin, and leaving a reddish-violet solution. Like the other bases already described, it does not expel ammonia from its salts. The salts of this base crystallise well, are easily decomposed, and easily soluble in water and alcohol.

The *hydrobromide*,  $C_{10}H_{13}NO.Br$ , forms colourless rhombic tables, which become violet on exposure to the air.

The *hydrochloride*,  $C_{10}H_{13}NO.HCl$ , crystallises in colourless acuminate rhombic prisms, often united in twin-growths.

The *platinochloride*,  $(C_{10}H_{13}NO.HCl)_2PtCl_4$ , crystallises in slightly yellow rhombic prisms; soluble in water and alcohol, but only sparingly soluble in a mixture of alcohol and ether.

The hydriodide crystallises in yellow tablets or prisms, and the oxalate in small colourless prisms.

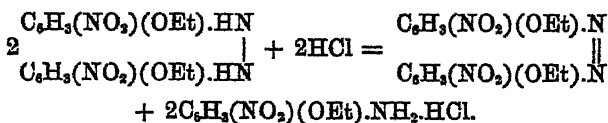
The attempts to prepare triethylammonium derivatives of orthamidophenetol and orthamidophenol have proved unsuccessful.

In conclusion, the author draws attention to the relations between the boiling points of these bases and those of the corresponding substituted anilines. The monethylamidophenetol boils  $7.5^{\circ}$  higher than the diethyl base, and monethylamidophenol  $10^{\circ}$  higher than the diethylphenol. The diethylorthamidophenetol has the same boiling point as orthamidophenetol. Ethylaniline boils  $10^{\circ}$  lower than diethylaniline.

P. P. B.

**Nitroorth- and Nitropara-azophenetols.** By H. ANDREAE (*J. pr. Chem.*, [2], 21, 318—341).—By the nitration of orthazophenetol, two dinitro-derivatives were obtained, which were separated by means of the difference of solubility in alcohol. The *dinitrazophenetol*,  $C_{10}H_{10}N_4O_6$ , which is soluble in alcohol, and forms about one-fourth of the yield, crystallises in bright reddish-yellow needles (m. p.  $190^{\circ}$ ). Its isomeride, which is insoluble in alcohol, crystallises from hot chloroform or benzene in lustrous brownish-red prisms (m. p.  $284$ — $285^{\circ}$ ), which under the microscope appear blue when viewed by reflected light. It sublimes with partial decomposition, and is not acted on by concentrated hydrochloric or nitric acid; concentrated sulphuric acid, however, dissolves it, forming a bright-red solution, from which it is thrown down by water as a yellow flocculent precipitate.

This dinitrazophenetol (m. p.  $284$ — $285^{\circ}$ ), when reduced by ammonium sulphide, yields a *dinitrohydrazophenetol*,  $C_{10}H_{12}N_4O_6$ , which is insoluble in water and in alcohol, sparingly soluble in boiling alcohol, and largely soluble in chloroform, benzene, and ether. It crystallises from concentrated alcoholic solutions in brilliantly lustrous prisms (m. p.  $201$ — $202^{\circ}$ ), and by slow evaporation from dilute solutions, it is obtained in long iridescent prisms, having a vitreous lustre. When heated for a considerable time in the water-bath with hydrochloric acid, it is resolved into dinitrazophenetol and nitramidophenetol hydrochloride—



At the same time a small quantity of a weak base is formed, the salts of which are decomposed by water.

*Nitramidophenetol*,  $C_6H_5(OEt)(NO_2).NH_2$ , prepared by decomposing the hydrochloride, obtained in the manner already described, with an alkali, and extracting with ether. It crystallises from aqueous alcohol in long yellow needles (m. p.  $96$ — $97^{\circ}$ ). It forms well crystallised salts. Nitrous acid converts it into a diazo-compound, which when boiled with alcohol yields paranitrophenetol, thus showing the compound to be a nitramidophenetol, and not a diphenyl-derivative;

further, that the dinitrazophenetol, which was prepared from orthazophenetol, has the constitutional formula,



And the dinitrohydrazo- and nitramido-phenetols contain the groups in similar positions.

Nitramidophenetol when heated with concentrated hydrochloric acid at  $155^\circ$ , is resolved into ethyl chloride and nitramidophenol.

Parazophenetol, prepared according to Schmitt's method (*J. pr. Chem.* [2], 18, 198), is scarcely acted on by cold concentrated nitric acid; both hot concentrated and fuming nitric acid attack it, forming (1) dinitrophenetol, soluble in water; (2) trinitrazoxyphenetol, soluble in alcohol, and an isomeride of the latter insoluble in alcohol. These three products were separated by the difference of solubilities in water and alcohol.

*Dinitrophenetol*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OEt}$ , crystallises from alcohol in white silky leaflets (m. p.  $85^\circ$ ), and is volatile in steam. It is sparingly soluble in hot water. When heated at  $150^\circ$  with concentrated hydrochloric acid in sealed tubes, it yields a dinitrophenol (m. p.  $102-103^\circ$ ). This is probably an isomeride of the  $\alpha$ - and  $\beta$ -dinitrophenols prepared by Hübner, melting at  $63-64^\circ$  and  $113-114^\circ$  respectively.

*Trinitrazoxyphenetol*,  $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_6$ , crystallises from alcohol in long fine yellow needles, united in stellate groups. It is sparingly soluble in alcohol, easily soluble in hot alcohol, ether, chloroform, benzene, and glacial acetic acid, and insoluble in water. The isomeride of this trinitro-derivative, which is insoluble in alcohol, dissolves in glacial acetic acid, chloroform, and benzene, and very easily in ethyl acetate, from which it crystallises in bright yellow needles (m. p.  $187^\circ$ ). It dissolves in concentrated sulphuric acid, and is reprecipitated from this solution by water. Nitric acid oxidises it with the production of the dinitrophenetol described above. Concentrated hydrochloric and hydrobromic acids do not act on it, whereas it is acted on by hydriodic acid. Alcoholic potash and soda also attack it. It is reduced by means of ammonium sulphide.

In conclusion, the author draws attention to the fact that the apparently abnormal behaviour of parazophenetol with nitric acid is similar to the behaviour of azobenzene and azotoluene when treated with nitric acid. (H. Petriew, *Ber.*, 6, 557.) P. P. B.

**Occurrence of Vanillin in certain kinds of Raw Beetroot Sugar.** By C. SCHEIBLER (*Ber.*, 13, 335-340).—The author finds that a substance (m. p.  $79^\circ$ ) identical with vanillin occurs among the soluble non-saccharine constituents of the juice of beetroot sugar, and especially in such as are neutral or slightly acid, but rarely in those which are strongly alkaline. T. C.

**Synthesis of Aromatic Aldehydes: Cuminaldehyde.** By A. ETARD (*Compt. rend.*, 90, 534-536).—The author has previously shown that the oxidation of cymene derived from terebenthene by chromic dichloride in solution in carbon bisulphide, yields an oil forming a crystalline compound with sodium hydrogen sulphite;

this, when decomposed by sodium carbonate, gives an aldehyde fusing at  $80^{\circ}$ , and resembling camphor in appearance. If the temperature be allowed to rise as high as the boiling point of the carbon bisulphide, the character of the reaction is completely changed.

Cymene and chromic dichloride, when dissolved in carbon bisulphide and mixed in the proportion of 1 mol. of the former to 2 mols. of the latter, give a chocolate-brown granular precipitate containing  $C_{10}H_{14} \cdot 2CrO_2Cl_2$ . This is decomposed by water with the production of cuminaldehyde which boils at  $223^{\circ}$  (uncorr.), and may be purified by combining it with sodium hydrogen sulphite and decomposing the compound formed by means of sodium carbonate. Benzoic, isocuminic, and anisic aldehydes may be easily obtained by this method. *The chromic dichloride attacks the group  $CH_3$  connected with the radicle phenyl, and by the further action of water transforms it into the group  $COH$ , characteristic of the aldehydes.*

Dimethylbenzene, oxidised in this manner, yields metamethylbenzaldehyde, which when purified boils at  $200^{\circ}$ .

In these reactions a small quantity of the corresponding chlorine-derivative is generally formed. The chromic acid produced by the action of the water on the chromic dichloride gradually oxidises the aldehydes if allowed to remain in contact with them. C. H. B.

**Action of Acetic Anhydride on some Aromatic Aldehydes.** By P. BARBIER (*Bull. Soc. Chim.* [2], 33, 52—56).—Three classes of acetyl-derivatives may be obtained from aromatic aldehydes: (1) in which the aldehyde function is destroyed by substitution; (2) in which the phenol function is destroyed by substitution; and (3) in which the substitution takes place in both functions. Bodies of the first class behave as monatomic phenols, those of the second class as monatomic aldehydes, and those of the third class as ethers. It is from the derivatives of the second class only that coumarin and its analogues can be obtained. The author's experiments have been made with salicylic aldehyde, paroxybenzoic aldehyde, and the two oxytoluic aldehydes formed by the action of chloroform on an alkaline solution of liquid cresol. These two bodies had been isolated in the pure state by him when the note of Tiemann and Schotten appeared. The liquid aldehyde boils at  $206$ — $208^{\circ}$ , the crystals of solid aldehyde melt at  $120^{\circ}$ . All these aldehydes, when heated in sealed tubes with excess of acetic anhydride at  $180^{\circ}$  for six hours, give acetyl-derivatives of the second class, of which acetosalicylol,  $C_6H_4(ACO) \cdot COH$ , is a type. The new bodies thus obtained by the author are—

*Acetylparoxybenzaldehyde*,  $C_6H_5O_3$ .—A colourless oily liquid (b. p.  $260^{\circ}$ ), with an odour like that of the phenyl acetate. It combines with sodium hydrogen sulphite.

*Acetyl derivative of liquid oxytoluic aldehyde*,  $C_{10}H_{10}O_3$ .—A colourless slightly oily liquid (b. p.  $267^{\circ}$ ), combining with sodium hydrogen sulphite. It does not solidify in a mixture of ice and salt.

*Acetyl derivative of solid oxytoluic aldehyde*,  $C_{10}H_{10}O_3$ .—A liquid similar to the preceding (b. p.  $275^{\circ}$ ). All these compounds, when boiled with baryta-water, yield the corresponding aldehyde and acetic acid. The reaction which gives rise to these acetic salts is similar

to that observed in the case of salicylic aldehyde. An acetate of the third class is first formed,  $C_6H_4(HO).COH + 2\text{Ac}_2O = C_6H_4(O\text{Ac}).C(O\text{Ac})_2H + \text{Ac.OH}$ . It may be isolated by prolonged washing of the product with sodium carbonate solution, and crystallises in fine white needles (m. p.  $100^\circ$ ). On treating this compound with potassium hydrate, the acetyl of the phenol portion is removed, and an ether of the first class produced,  $C_6H_4(O\text{Ac}).C(O\text{Ac})_2H + KOH = C_6H_4(OH)C(O\text{Ac})_2H + KO\text{Ac}$ . Diacetic salicylol forms large colourless crystals (m. p.  $104-105^\circ$ ). On the other hand, by distilling the original acetyl-derivative, an ether of the second class is produced,  $C_6H_4(O\text{Ac}).C(O\text{Ac})_2H = \text{Ac}_2O + C_6H_4(O\text{Ac}).COH$ .

J. M. H. M.

**Action of Nascent Hydrogen on Orthonitrobenzaldehyde.** By C. RUDOLPH (*Ber.*, 13, 310-311).—Orthonitrobenzaldehyde, on treatment with tin and glacial acetic acid, gives a base,  $C_6H_5N$ , which crystallises in colourless plates. Its constitution is most probably

represented by the formula 
$$\begin{array}{c} \text{N} \\ || \\ \text{H} \text{C} \end{array} \text{C}_6\text{H}_5.$$

A monochlorinated derivative of this base is obtained by the action of stannous chloride and hydrochloric acid on orthonitrobenzaldehyde. It melts at  $83^\circ$ , and forms a hydrochloride,  $C_6H_4ClN.HCl.H_2O$ , which crystallises in reddish-coloured plates. The author is continuing his investigation.

T. C.

**Formation of Cinnamic Aldehyde during Fibrin-pancreas Digestion.** By J. OSSIKOVSKY (*Ber.*, 13, 326-328).—The author has found cinnamic aldehyde among the volatile products obtained by fibrin-pancreas digestion, and considers that this fact accounts for the formation of phenylpropionic and phenylacetic acids by the putrefaction of albuminous substances as observed by the Salkowskis.

T. C.

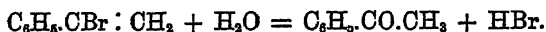
**Limited Oxidation of Ethylbenzene.** By C. FRIEDEL and M. BALSCHN (*Bull. Soc. Chim.* [2], 2, 615-617).—The sole aromatic product of the oxidation of ethylbenzene, according to the observations of Fittig and of Kekulé, is benzoic acid. All the attempts made by Kekulé to obtain an intermediate aldehyde,  $C_6H_5.CH_2.CO.H$ , were unsuccessful. The authors show that the  $CH_2$  group is the first to oxidise, the product of incomplete oxidation being methylphenylketone. This substance is produced by the action of chromic acid in insufficient quantity on ethylbenzene in acetic solution. The reaction is complete in about fifteen minutes, and the mixture must be cooled in water to prevent too rapid action. Twenty grams of ethylbenzene furnished about 2 grams of methylphenylketone obtained in a pure state by agitating the oxidised mixture with water and fractionally distilling the supernatant liquid.

J. M. H. M.

**Conversion of Bromostyrolene into Methylphenylketone.** By C. FRIEDEL and M. BALSCHN (*Bull. Soc. Chim.* [2], 32, 613-615). By the action of sodium and carbonic anhydride on the bromostyrolene obtained from styrolene bromide by treatment with alcoholic



potash, Swarts obtained cinnamic acid, and hence assigned the formula  $\text{PhCH}:\text{CHBr}$  to bromostyrolene. The authors, however, show that the formula  $\text{PhCBr}:\text{CH}_2$  is the correct one, since by the action of sulphuric acid or water on this substance, methylphenylketone is produced, just as acetone is obtained from chloropropylene,  $\text{MeCCl}:\text{CH}_2$ . The reaction of bromostyrolene with sulphuric acid yields methylphenylketone in very small quantity, but about 66 per cent. of the theoretical proportion can be easily obtained by heating bromostyrolene in sealed tubes with a large excess of water at  $180^\circ$  for 12 hours.



By means of this reaction, methylphenylketone can be obtained from ethylbenzene. The authors explain the production of cinnamic acid in Swart's experiments by supposing either that the crude bromostyrolene contains  $\text{PhCH}:\text{CHBr}$ , as well as  $\text{PhCBr}:\text{CH}_2$ , or that the acid  $\text{C}_6\text{H}_5.\text{C}:\text{C}.\text{COOH}$  is formed first, and that this becomes cinnamic acid by fixation of hydrogen.

J. M. H. M.

**Isophthalophenone.** By E. ADOR (*Bull. Soc. Chim.* [2], 33, 56—59).—This substance was prepared by treating isophthalic chloride with benzene in presence of aluminium chloride; the product was washed with water, the excess of benzene distilled off, and the product treated with dilute soda. The residue is isophthalophenone, and the solution contains sodium isophthalate and the sodium salt of an acid which melts at  $161^\circ$ , and is less soluble in boiling water than isophthalic acid. The barium salt of the new acid crystallises in scales having the formula  $(\text{C}_{10}\text{H}_6\text{O}_3)_2\text{Ba} + 2\text{Aq}$ . The silver salt is very slightly soluble in boiling water, easily soluble in ammonia, and crystallises in white filaments, of the formula  $\text{C}_{10}\text{H}_6\text{O}_3\text{Ag}$ . The reaction of isophthalic chloride with benzene therefore takes place in two stages:—

- (1)  $\text{C}_6\text{H}_4(\text{COCl})_2 + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4(\text{COPh}).\text{COCl} + \text{HCl}$ ;
- (2)  $\text{C}_6\text{H}_4(\text{COPh}).\text{COCl} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4(\text{COPh})_2 + \text{HCl}$ .

The benzoylbenzoic acid obtained in the first of the above reactions is a *meta*-derivative; the acid melting at  $194^\circ$ , obtained on oxidising tolylphenylketone, is a *para*-derivative: therefore Plascuda and Zincke's acid melting at  $127$ — $128^\circ$ , obtained by oxidising benzyltoluene should be the *ortho*-acid.

Isophthalophenone, purified by distillation, boils at about  $260^\circ$ ; crystallised repeatedly from alcohol, it melts at  $99.5$ — $100^\circ$ . Treated with alcoholic potash or soda, it furnishes a reddish resin, insoluble in alcohol and water. Baeyer, by treating phthalophenone with soda, obtained triphenylmethane-carboxylic acid,  $\text{CH}(\text{C}_6\text{H}_5)_3.\text{C}_6\text{H}_4.\text{COOH}$ . Fused with potash, isophthalophenone furnishes benzoic acid, but no isophthalic acid. Treated with hot fuming nitric acid, it gives two isomeric derivatives:  $\alpha$ -dinitroisophthalophenone,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{COPh})_2$ , melts at about  $260^\circ$ , is almost insoluble in boiling alcohol, and crystallises from glacial acetic acid:  $\beta$ -dinitroisophthalophenone is formed at a lower temperature, melts at about  $100^\circ$ , is more soluble in alcohol and in acetic acid than the  $\alpha$ -derivative, but does not crystallise.

*β-Diamidoisophthalophenone*, obtained by reducing an acetic solution of the corresponding nitro-compound with metallic tin, is a yellowish amorphous powder, fusing at about 100°, but partially decomposing at about 70°, soluble in alcohol and in acetic acid, giving a reddish coloration, which is diminished by addition of hydrochloric acid. By the action of potassium nitrite on this compound, isophthalein appears to be formed.

*α-Diamidoisophthalophenone* behaves like the *β*-derivative, and appears also to give a phthalein. On reducing isophthalophenone with phosphorus and hydriodic acid at 200°, a colourless hydrocarbon is obtained, distilling above 360°, easily soluble in ether, slightly soluble in cold alcohol, and separating from boiling alcohol as a thick oil, which does not crystallise at -18°. Baeyer considers that when phthalic chloride is treated with benzene, it is the oxygen of the former which is replaced by phenyl groups, whereas the above experiments show that in the case of isophthalic chloride, it is the chlorine atoms that are replaced.

To escape this anomaly, the author suggests for phthalic chloride the formula  $C_6H_4 < \begin{smallmatrix} CCl_2 \\ CO \end{smallmatrix} > O$ , in place of that usually received.

J. M. H. M.

**Solubility of Benzoic and Salicylic Acids.** By E. BURGON (*J. Pharm. Chim.* [4], 30, 488—490).—According to Ost (*J. pr. Chem.* [2], 17, 288) 1 part benzoic acid is dissolved by 640 parts of water at 0°, and 1 part salicylic acid by 1,050—1,100 parts water. In reply, the author confirms his previous results (*ibid.* [4], 27, 528, and 29, 10), that at 0° 1 part of the former acid requires 580 water, and salicylic acid, 666.

The solubility of these acids from 0° to 35° may be represented by parabolic curves, and may be expressed by algebraic formula in functions of the temperature, that for salicylic acid being  $x_t = 0.002(t^2 + 10t + 750)$ , which at 0° gives  $x = 1.5$ , i.e., 1 liter of water dissolves 1.5 grams salicylic acid instead of 1 gram as stated by Ost.

L. T. O'S.

**Dinitrobenzoic Acid.** By F. BEILSTEIN and A. KURBATOW (*Ber.*, 13, 355).—Metadinitrobenzoic acid (m. p. 202°) is obtained by the oxidation of either *α*- or *β*-dinitronaphthalene. *Ethyl metadinitrobenzoate*,  $C_6H_3(NO_2)_2.COOEt$ , crystallises in brilliant colourless needles (m. p. 91°); 100 parts of alcohol (90 per cent.) dissolve 0.562 part of the salt at 13°. The formation of this ether serves as a ready method for detecting the acid.

T. C.

**Phenyl-lactic Acid.** By E. ERLKENMEYER (*Ber.*, 13, 303—305).—Glaser's phenyl-lactic acid (m. p. 93°) is phenyl-*β*- and not phenyl-*α*-hydroxypropionic acid, and has therefore the constitution—



*Phenyl-α-hydroxypropionic acid*,  $CH_3Ph.CH(OH).COOH$  (m. p. = 98°) is obtained from phenylethylaldehyde and hydrocyanic acid by the general reaction with hydrochloric acid. It is less soluble in water

than the  $\beta$ -acid, and a similar remark applies to the zinc salts of the two acids. When heated with dilute sulphuric acid in sealed tubes, it remains unaltered at  $100^\circ$ , but at  $130^\circ$  it splits up into phenyleth-aldehyde and formic acid, and at  $200^\circ$  it gives carbonic oxide, sulphurous anhydride, and a condensation-product of phenyleth-aldehyde,  $C_{24}H_{20}O_2$ , which crystallises in silky plates (m. p. =  $102^\circ$ ). The  $\beta$ -acid on the other hand is decomposed by dilute sulphuric acid at  $100^\circ$  into cinnamic acid, styrolene, cinnamic acid, and carbonic anhydride.

These facts show that in the hydrohalogen addition-products of cinnamic acid, the halogen must be in the  $\beta$ -position. This would explain the formation of styrolene from a phenylhalogen-propionic acid on treatment with sodium carbonate. T. C.

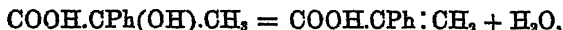
**Phenylbromolactic Acid.** By E. ERLKENMEYER (*Ber.*, 13, 305—310).—The author adduces facts which show that Glaser's phenyl oxyacrylic acid (*Annalen*, 147, 98) is a true oxy-acid, which stands to phenyldibromopropionic acid in the same relation that ethylene oxide does to ethylene bromide, and that the oxystyrolene obtained by Glaser (*loc. cit.*) from the above phenyloxyacrylic acid is phenyleth-aldehyde. T. C.

**Artificial Formation of Tropic Acid.** By A. LADENBURG and L. RÜGHEIMER (*Ber.*, 13, 373—379).—Hydratropic acid when oxidised with an alkaline solution of potassium permanganate gives atrolactic acid, thus:— $CHPhMe.COOH + O = CPhMe(OH).COOH$ , and this fact, taken in conjunction with the results of R. Meyer (*Ber.*, 11, 1283, 1787) on the hydroxylation of acids which contain the CH-group in the side-chain, would seem to show that tropic acid has the constitution assigned to it in the foregoing equation, and not—

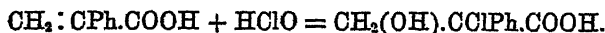


as ascribed to it by Fittig and Wurster (*Annalen*, 195, 145). If this be true, then tropic acid must be represented by the last-named formula.

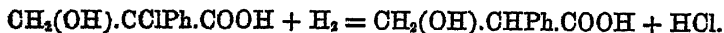
Atrolactic acid on boiling with concentrated hydrochloric acid gives atropic acid,  $C_9H_8O_2$  (m. p. =  $106^\circ$ ), thus:—



which shows that atrolactic acid is not identical with Glaser's phenyl-lactic acid, for the latter under similar circumstances gives cinnamic acid. By the action of hypochlorous acid atropic acid is converted into *chlortropic acid*,  $C_9H_7ClO_2$  (m. p. =  $129^\circ$ ), thus:—



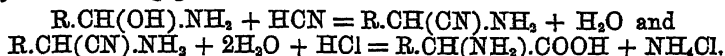
Chlortropic acid is very soluble in water, and on reduction with zinc dust and iron filings in an alkaline solution, gives tropic acid (m. p.  $118^\circ$ ), thus:—



We have thus passed by a series of reactions from hydratropic acid to tropic acid, and the authors hope that by the synthesis of one of this

series of compounds to be able to settle finally the constitution of all of them. T. C.

**Aromatic Amido-Acids.** By F. TIEMANN and L. FRIEDLÄNDER (*Ber.*, 13, 381—385).—Strecker (*Annalen*, 75, 27) prepared alanine by the following general reactions:—



The intermediate amido-cyanide,  $\text{R.CH(CN).NH}_2$ , can, however, be better obtained from the aldehydcyanhydrin, by the action of ammonia, thus:— $\text{R.CH(CN).OH} + \text{NH}_3 = \text{R.CH(CN).NH}_2 + \text{H}_2\text{O}$ , and this reaction is applicable not only to the acetic acid series, but also to aromatic aldehydes and even to ketones.

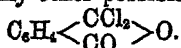
*Phenyl-amidoacetic acid*,  $\text{C}_6\text{H}_5(\text{NH}_2).\text{COOH}$ , is obtained by digesting 1 mol. of benzaldehydcyanhydrin with 1 mol. of ammonia dissolved in absolute alcohol at 60—80°. It crystallises in prisms or sometimes in six-sided tables (m. p. 256°), which are only sparingly soluble in cold, but more soluble in hot water. It is sparingly soluble in alcohol, but more easily in ether. On distillation, it yields an oil which becomes crystalline on standing (m. p. below 100°). Distilled with lime, it gives benzylamine; it forms crystalline copper and lead compounds, and a hydrochloride which crystallises in prisms, and is soluble in water. These facts show that this acid is identical with the amido-acid obtained by Stöckenius (*Ber.*, 11, 2002) from phenyl-bromacetic acid and ammonia. T. C.

**Oxidation of Sulphaminemetatoluic Acid.** By I. REMSEN (*Ber.*, 13, 347—351).—The author maintains the correctness of his statement (*ibid.*, 11, 1328, 2088), that sulphaminemetatoluic acid gives sulphoisophthalic acid on oxidation, and denies the validity of Jacobsen's conclusions to the contrary. He also shows that Jacobsen's assertion, that Lassaigne's reaction is not applicable to the detection of nitrogen in bodies containing sulphur, is incorrect, and that the method proposed by Jacobsen for this purpose, viz., the substitution of iron filings for sodium, cannot be depended on. T. C.

**Constitution of Tyrosine and Skatole.** By J. OSSIKOVSKY (*Ber.*, 13, 328—334).

**Constitution of Phthalic Chloride.** By E. v. GERICHTEN (*Ber.*, 13, 417—422).—There are two possible formulæ for phthalyl chloride, viz.:— $\text{C}_6\text{H}_4(\text{COCl})_2$ , and  $\text{C}_6\text{H}_4\langle \begin{smallmatrix} \text{COCl} \\ \text{CO} \end{smallmatrix} \rangle \text{O}$ , but it has not yet been definitely settled which of these is correct (comp. this vol., p. 471). The present investigation was begun with the object of throwing further light on this subject. Phthalide, although not attacked by chlorine at a boiling temperature, is easily decomposed by phosphorus pentachloride, even at 60—80°, with the formation of a compound,  $\text{C}_6\text{H}_4\text{Cl}_4\text{O}$ , consisting of large monosymmetric crystals (m. p. 88°, b. p. = 275°, with slight decomposition), which are readily soluble in alcohol, ether, and in light petroleum, but insoluble in water. It is not acted on by

boiling water, and only slowly by boiling potash, but when gently heated with concentrated sulphuric acid, it is easily decomposed into hydrochloric acid and phthalic acid. It reacts with phenol, forming hydrochloric acid and phenyl phthalate (m. p. 70°). A compound,  $C_6H_4Cl_4O$ , isomeric with the above (m. p. 88°), is obtained, together with a smaller quantity of the latter when 1 mol. of phthalic chloride is heated with rather more than 1 mol. of phosphorus pentachloride in sealed tubes at 210–220° for 50 hours. It crystallises in colourless tables (m. p. 47°, b. p. 262°, with slight decomposition), and in most of its chemical properties it has great resemblance to its isomeride (m. p. 88°). Both compounds, when treated with aniline, give the same product, which crystallises from hot alcohol in brilliant yellow scales (m. p. 152°), soluble in cold alcohol, more easily in hot alcohol, readily soluble in ether, and in chloroform, less so in light petroleum, and insoluble in water. It is reprecipitated by water unchanged from its solution in concentrated hydrochloric acid or glacial acetic acid. On heating with concentrated hydrochloric acid, alcoholic potash, or aqueous ammonia, it gives phthalic acid and aniline. Analysis led to the formula  $C_6H_4 \begin{smallmatrix} \text{CNPh} \\ \text{CO} \end{smallmatrix} \text{—} \text{NPh}$ . It is shown that the difference between the two bodies,  $C_6H_4Cl_4O$ , cannot be due to physical metamorphism or to polymerism; and it seems most probable that the one (m. p. 88°) is  $C_6H_4 : (CCl_2)_2 : O$ , and the other (m. p. 47°)  $C_6H_4(CCl_2).COCl$ . Since phthalic chloride gives both these compounds, it cannot have the constitution  $C_6H_4(COCl)_2$ , as such a body could not yield a substance having the second of the above formulæ: hence it must have the only other possible constitution, viz.:—



T. C.

**A New Series of Dye-stuffs.** By E. FISCHER (*Ber.*, 13, 317–319).—Phenanthrenedisulphonic acid, when treated with phenols, and more especially with resorcinol, gives a series of condensation-products, having the properties of dye-stuffs, very similar to the phthaleins described by Baeyer. In the case of resorcinol, the product (*phenanthrenesulphlein-resorcin*,  $C_{22}H_{16}O_7S_2$ ) is a brittle mass, with a cantharidian lustre, yielding a dark red-brown powder. Its solution, especially in alkalis, exhibits a fluorescence greater than that of fluorescein, and by transmitted light has a blood-red, and by reflected light a green colour. A constitution analogous to that of resorcinphthalein is ascribed to this substance, viz.:— $O \begin{smallmatrix} \text{C}_6H_3(OH) \\ \text{C}_6H_3(OH) \end{smallmatrix} > O.S_2C_{14}H_8$ .

It is sparingly soluble in cold water, but more easily soluble in hot, giving a golden-yellow liquid; it is still more easily soluble in alcohol. These solutions dye silk yellow, whilst its alkaline solution dyes red. It combines with bromine to form a dark violet-red powder, which is less soluble in water than the sulphlein, but more soluble in hot alcohol; this bromine derivative gives a bluish-red solution with alkalis, which imparts the same colour to silk. Both the sulphlein and its bromo-derivative become colourless on reduction. With rosaniline in alcoholic solution, the sulphlein gives a characteristic cherry-

red liquid, which dyes silk a beautiful red. The bromo-compound gives a bluish product when treated in a similar manner.

With pyrogallol, phenanthrenedisulphonic acid gives a body which dissolves in alkalis with a brown-red colour. The author proposes to utilise the fact of the production of these coloured compounds in the detection of a disulphonic acid in the presence of the mono-acid. A method is described for preparing phenanthrenedisulphonic acid on the large scale, and as a source of the above-mentioned dye-stuffs.

T. O.

**Potassium Hydrindigotin-Sulphate and Potassium Indoxylsulphate.** By E. BAUMANN and F. TIEMANN (*Ber.*, 13, 408—415).—This is a reply to Baeyer's remarks on a previous communication of the authors (*Ber.*, 12, 1098—1192), in which they had advanced the opinion that hydrindigotin-sulphuric acid and indoxylsulphuric acid were not identical as stated by Baeyer. Further experiments now confirm their first conclusions.

Potassium hydrindigotin-sulphate is best obtained by dissolving about 25 grams of moist but well-pressed hydrindigotin (indigo-white) in 25 grams of a solution of potash (1:2), a current of hydrogen being simultaneously passed through the liquid; the latter is then decomposed by the addition of 12—15 grams of potassium pyrosulphate and continuous shaking with air for an hour. The filtrate, after agitation with ether, is mixed with alcohol to get rid of the bulk of the sulphate, the remainder being removed by means of barium chloride. The quantity of the potassium hydrindigotin-sulphate formed was in all cases very small. A comparison of solutions of the potassium salts of hydrindigotin-sulphuric acid and indoxylsulphuric acid gave the following results:—(1.) Both solutions remain unchanged when agitated in contact with air. (2.) On the addition of dilute hydrochloric acid to the hydrindigotin-sulphate solution, indigo-white is at once thrown down, and this, on agitation with air or by treating with a small quantity of ferric chloride, is oxidised to indigo-blue. The indoxylsulphate, on the other hand, remains unchanged on the addition of dilute hydrochloric acid, and on warming an oil of faecal odour is precipitated, which after some time changes to a red amorphous substance, soluble in alcohol and in ether. If ferric chloride is not added previous to treating with dilute hydrochloric acid, this compound contains only a very small quantity of indigo. This very different behaviour of the potassium salts of the two acids towards hydrochloric acid serves as a very ready method of separating the two when present together in solution. (3.) Indigo-blue is at once precipitated when a solution of the hydrindigotin-sulphate is decomposed with a mixture of ferric chloride and hydrochloric acid; whereas the indoxylsulphate, under similar conditions, does not give a precipitate of indigo until it is warmed. The aqueous or alcoholic solution of the hydrindigotin sulphate is decomposed on evaporation, even in the presence of an excess of alkali, with the separation of indigo; whereas the indoxylsulphate does not undergo decomposition either on repeated evaporation or even by heating with excess of alkali in sealed tubes at 160°. These facts show conclusively that the two acids are not identical as stated by Baeyer.

The urine of rabbits fed with food containing finely powdered indigo gives a precipitate of indigo on the addition of a few drops of hydrochloric acid, and the filtrate, like the normal urine, gives Jaff's indican reaction. The urine of dogs fed in a similar manner does not give indigo on addition of hydrochloric acid, but it does if fed with damp indigo-white wrapped in paper. These experiments show that, in virtue of some powerful reducing action in the intestines of the rabbit, the indigo is partially reduced to indigo-white; whilst in the case of dogs such a strong reducing action does not occur. When rabbits are fed for a long time with indigo, symptoms of palsy set in, and the urine becomes albuminous; whilst in the loins a considerable deposit of indigo takes place, showing that the indigo-white first formed is reconverted into indigo, and in great part, therefore, does not behave like other phenol compounds forming ethereal sulphates. In the cases of animals fed with indol, and whose urine then contains potassium indoxylsulphate, similar phenomena are not observed. The above experiments, although not conclusive, render it very probable that a salt of hydrindigotin-sulphuric acid is present in the urine of animals fed with indigo-white.

T. C.

**Sulphur-derivatives of Diphenyl.** By S. GABRIEL and A. DEUTSCH (*Ber.*, 13, 386—391). — *Diphenylmonosulphonic chloride*,  $C_{12}H_{10}.SO_2Cl$ , is obtained by treating potassium diphenylmonosulphonate with an equivalent quantity of phosphorus pentachloride. It crystallises in pale yellow prisms (m. p.  $115^\circ$ ), which are soluble in alcohol, ether, and carbon bisulphide. Digestion with alcoholic ammonia in sealed tubes at  $100^\circ$  converts it into *diphenylmonosulphamide*,  $C_{12}H_{10}.SO_2NH_2$ , which crystallises in needles (m. p.  $228^\circ$ ), and is easily soluble in ether and carbon bisulphide, but almost insoluble in water and in benzene.

*Diphenyl mercaptan*,  $C_{12}H_{10}.SH$ , is obtained from the sulphonic chloride by reduction with tin and hydrochloric acid, and subsequent distillation in steam. It is a white mass (m. p.  $110^\circ$ ), which, when freshly prepared, is completely soluble in alkalis, but on keeping gradually loses this property, owing to its conversion into the disulphide by the action of the air; it is soluble in alcohol, glacial acetic acid, and ether, and more easily in benzene and carbon bisulphide; it forms crystalline mercaptides with lead and mercury.

*Diphenyl sulphide* ( $C_{12}H_{10}$ ) $_2S$ , is obtained by the dry distillation of the lead mercaptide. It crystallises in brilliant plates (m. p.  $= 171^\circ$ ), which are moderately soluble in alcohol, ether, glacial acetic acid, carbon bisulphide, and benzene.

*Diphenyl sulphone* ( $C_{12}H_{10}$ ) $_2SO_2$ , is formed by the oxidation of diphenyl sulphide with potassium permanganate in glacial acetic acid solution. It crystallises in colourless plates (m. p.  $= 215^\circ$ ), and is easily soluble in alcohol, carbon bisulphide, and benzene, but only sparingly soluble in ether. A compound, apparently identical with this sulphone, may be prepared by heating diphenylsulphonic chloride with diphenyl in the presence of aluminium chloride.

*Diphenyl disulphide* ( $C_{12}H_{10}$ ) $_2S_2$ , is the product obtained by the spontaneous oxidation of diphenyl mercaptan. It is, however, more con-

veniently prepared by employing dilute nitric acid as the oxidising agent. It crystallises in colourless needles (m. p.  $149^{\circ}$ ), which are easily soluble in alcohol and carbon bisulphide, but less soluble in ether or glacial acetic acid.

*Diphenylmonosulphinic acid*,  $C_{12}H_{10}SO_2H$ , is obtained, together with diphenyl and the following compounds, by the reduction of an ethereal solution of the monosulphonic chloride with sodium amalgam. It is a crystalline powder, which is decomposed even at  $70^{\circ}$ , and is soluble in hot water.

*Ethyl diphenylmonosulphonate*,  $C_{12}H_{10}SO_2Et$ , obtained as above described or by the action of ethyl iodide on the corresponding silver salt, crystallises in needles (m. p.  $= 73^{\circ}$ ), which are easily soluble in dilute alcohol, ether, carbon bisulphide, and benzene.

*Trisulphondiphenyl hyponitrite* ( $C_{12}H_{10}SO_3$ )<sub>2</sub>NO is formed, together with diphenylmonosulphonic acid, by oxidising diphenylmonosulphonic acid with dilute nitric acid. It crystallises in needles (m. p.  $178^{\circ}$ ), which are but sparingly soluble in ether, benzene, or carbon bisulphide.

*Diphenyl sulphocyanide*,  $C_{12}H_{10}S.CN$ , is prepared, together with the bisulphide, by the action of an ethereal solution of cyanogen iodide on the lead mercaptide at  $100^{\circ}$ . It has not yet been obtained in a pure state. The impure substance melts at about  $84^{\circ}$ .

*Diphenylmonosulphacetic acid*,  $C_{12}H_{10}S.CH_2.COOH$ , is obtained by mixing the mercaptan with monochloroacetic acid, each being dissolved in caustic soda. The acid (m. p.  $169^{\circ}$ ) is sparingly soluble in water and in alcohol, but more easily in carbon bisulphide, benzene, and ether.

*Diphenyldisulphonic chloride*,  $C_{12}H_{10}(SO_2Cl)_2$ , is obtained by the action of phosphorus pentachloride on potassium diphenyldisulphonate. It crystallises in lustrous prisms (m. p.  $203^{\circ}$ ), soluble in alcohol, ether, and benzene, but less soluble in carbon bisulphide.

*Diphenyldisulphamide*,  $C_{12}H_{10}(SO_2NH_2)_2$ , prepared like the monosulphamide, crystallises from boiling water in slender white colourless needles (m. p. above  $300^{\circ}$ ), which are only sparingly soluble in alcohol and benzene, but more easily in carbon bisulphide or ether.

*Diphenyl disulphhydrate*,  $C_{12}H_{10}(SH)_2$ , prepared by reduction of the disulphonic chloride with tin and hydrochloric acid. It forms colourless plates (m. p.  $176^{\circ}$ ), which are soluble in alcohol, ether, and carbon bisulphide, and still more easily in benzene. It forms a brown mercaptide with lead.

*Diphenyldisulphacetic acid*,  $C_{12}H_{10}(S.CH_2.COOH)_2$ , obtained like the corresponding mono-compound, forms crystals (m. p.  $= 252^{\circ}$ ), which are sparingly soluble in water and alcohol, and almost insoluble in carbon bisulphide, benzene, and ether.

Diphenyldisulphonic acid, on reduction with sodium-amalgam, does not give a disulphinic acid, but diphenyl and diphenylmonosulphonic acid.

T. C.

**Dinitronaphthalene.** By F. BEILSTEIN and A. KURBATOW (*Ber.*, 13, 353—354).— $\alpha$ -Dinitronaphthalene, on oxidation with dilute nitric acid in sealed tubes at  $150^{\circ}$  gives ordinary nitrophthalic acid, together



with ordinary dinitrobenzoic acid and a little picric acid.  $\beta$ -dinitronaphthalene under similar circumstances gives dinitrophthalic acid, dinitrobenzoic acid, and a little picric acid.

*Dinitrophthalic acid*,  $C_8H_2(NO_2)_2(COOH)_2$ , crystallises in large prisms (m. p.  $226^\circ$ ), which are easily soluble in water, alcohol, and ether, but insoluble in carbon bisulphide, low boiling petroleum, or benzene. The *calcium* salt,  $C_8H_2N_2O_8Ca$ , is sparingly soluble in water. The *barium* salt,  $C_8H_2N_2O_8Ba$ , is a crystalline precipitate, which is insoluble in water and dilute acetic acid. *Ethyl dinitrophthalate*,  $C_8H_2(NO_2)_2(COOEt)_2$ , crystallises in needles (m. p.  $186^\circ$ ), which are easily soluble in alcohol, but less so in chloroform. T. C.

**Condensation of Benzhydrol and Naphthalene.** By A. LEHNE (*Ber.*, 13, 358—360).—*Naphthylidiphenylmethane*,  $C_{23}H_{18}$ , is obtained by heating 10 parts of benzhydrol and 15 parts of naphthalene with 15 parts of phosphoric anhydride in an oil-bath at  $140$ — $145^\circ$  for several hours. According to the process employed and the amount of solvent used, two sets of crystals may be obtained, the one melting at  $134^\circ$  and the other  $149^\circ$ ; the first modification is easily converted into the second either by recrystallisation or by fusion. The hydrocarbon is only sparingly soluble in absolute alcohol and in light petroleum, more easily in ether, and in glacial acetic acid, and very easily in benzene; it sublimes without decomposition. On oxidation, it gives an acid in small yellow crystals (m. p.  $= 206^\circ$ ), which has not yet been completely investigated.

*$\alpha$ -Naphthylphenyl carbinol*,  $C_{17}H_{14}O$ , is obtained by the reduction of  *$\alpha$ -naphthylphenylketone* in alcoholic solution with sodium amalgam. It forms nodular crystals (m. p.  $86^\circ$ , b. p. over  $360^\circ$ ), which are readily soluble in alcohol, ether, and benzene, but only sparingly soluble in light petroleum. On treatment with concentrated sulphuric acid or phosphoric anhydride, it gives beautiful violet-blue condensation products; but by the action of phosphoric anhydride in sealed tubes at  $120^\circ$ , either with or without the presence of benzene, it gives  *$\alpha$ -naphthylphenylketone*, and not naphthylidiphenylmethane as was expected. By incomplete reduction with sodium amalgam,  *$\alpha$ -naphthylphenylketone* gives a compound crystallising in needles (m. p.  $61^\circ$ ). T. C.

**Phenanthrenedisulphonic Acid and its Derivatives.** By E. FISCHER (*Ber.*, 13, 314—316).—*Phenanthrenedisulphonic acid*,  $C_{14}H_8(SO_3H)_2$ , (compare Græbe, *Annalen*, 167, 152, and Rehs, *Ber.*, 10, 1252), is obtained by adding one part of phenanthrene gradually and with continual shaking to four parts of pyrosulphuric acid, and then allowing the liquid to stand for about half an hour on a water-bath. It forms a yellowish-brown non-crystallisable syrup. Its salts, including the barium salt, are, as a rule, easily soluble in water, but insoluble in alcohol and ether. The potassium salt when distilled with potassium cyanide, or better with dry potassium ferrocyanide, gives the nitril, and a substance which crystallises in white needles, and is only sparingly soluble in alcohol. The *nitril* crystallises in bright yellow plates, which are easily soluble in hot alcohol; on saponification it gives an acid which with resorcinol yields a body which has great

resemblance to Baeyer's fluoresceïn; this same substance was also obtained by fusing the potassium disulphonate with sodium formate. It is still under investigation. T. C.

**Electrolysis of Terebenthene.** By A. RENARD (*Compt. rend.*, 90, 531—534).—When a solution of terebenthene (25 c.c.) in alcohol (80 c.c.) is mixed with sulphuric acid diluted with an equal volume of water (20 c.c.), and subjected to the prolonged action of a powerful electric current, hydrogen is evolved at the negative pole, but no gas appears at the positive pole. The addition of water to the liquid causes the separation of a dark-coloured oil, which consists of ethyl acetate, formed by oxidation of the alcohol, a small quantity of unattacked terebenthene, cymene boiling between 178—180°, and *tere-benthene monohydrate*,  $C_{10}H_{18}O$ , a yellowish, somewhat oily liquid, boiling between 210 and 214°; sp. gr. at 10° 0.9511; vapour-density 5.191. This compound is insoluble in water, but dissolves in alcohol, ether, and acetic acid. Oxygen gas is without action on it even after prolonged contact. It is attacked by bromine with great violence, hydrobromic acid being evolved. If, however, the bromine and the terebenthene monohydrate be both dissolved in carbon bisulphide before mixing, no hydrobromic acid is given off, but water is formed, together with a compound which could not be isolated, but which probably has the composition  $C_{10}H_{16}Br_2$ . This substance is decomposed on evaporation of the carbon bisulphide, and the residue when distilled with zinc-dust yields cymene. Terebenthene monohydrate is dissolved by concentrated sulphuric acid with deep brown colour. On the addition of water a black viscid mass separates out. When distilled with phosphoric anhydride the monohydrate yields terebenthene. It forms no hydrochloride with hydrochloric acid, and is not acted on by anhydrous acetic acid. Concentrated nitric acid attacks it with great violence, but the moderately dilute acid gives rise to oxalic acid and *cumidic acid*,  $C_{10}H_{10}O_4 + H_2O$ , slightly soluble in water, but soluble in alcohol. From these reactions, it would appear that terebenthene monohydrate is a pseudo-alcohol,  $C_{10}H_{18}H.OH$ .

The aqueous liquid from which the oil had been separated contained (1) terpin; (2) an acid forming a lead salt of the composition  $C_{12}H_{22}SO_7Pb$ ; this may be regarded as the lead-salt of a sulpho-ethylic derivative of hydroxycampholic acid,  $C_{10}H_{20}O_4$ , and probably has the constitution  $Pb<\begin{smallmatrix} CO_2 \\ SO_3 \end{smallmatrix}>C_8H_{17}.COOEt$ . (3) An acid giving a lead-salt of the composition C 38.84, H 8.04, S 11.14, Pb 14.40.

C. H. B.

**Podophyllin.** By I. GUARESCHI (*Gazzetta*, 10, 16—20).—The author has examined the podophyllin of commerce obtained from *Podophyllum peltatum*, and finds that it consists of two substances, a resin soluble in ether, and a glucoside which is not soluble in ether. This glucoside is decomposed by the action of emulsin, or when boiled with dilute sulphuric acid; in the latter case, the solution on cooling deposits a white powder, whilst the sugar remains dissolved. The product of the decomposition of the glucoside is soluble in alcohol and

also in boiling water, being deposited again as the solution cools; it has not been examined.

When commercial podophyllin is fused with potash and treated in the usual way, it yields a small quantity of a product, which seems to contain hydroxysalicylic acid, parahydroxybenzoic acid, and pyrocatechol.

The author considers that the glucoside in podophyllin resembles convolvulin and turpethin. C. E. G.

**Bases of the Pyridine Series.** By A. RICHARD (*Bull. Soc. Chim.* [2], 32, 486—489).—The author has undertaken the study of these bases, and especially of collidine, with a view to determine whether the pyridine, picoline, and collidine which occur in Dippel's animal oil, are identical or isomeric with bases of the same composition which have recently been prepared synthetically. 200 kilos. of bone-oil were digested with sulphuric acid, the acid liquor boiled to remove pyrrol, saturated with soda, and distilled in a current of steam: 2 kilos. of crude bases were obtained, from which the pyridine, picoline, lutidine, and collidine were easily isolated by fractional distillation in an apparatus with eight washers. In order to separate the higher bases (boiling above  $180^{\circ}$ ) it was necessary to conduct the distillation under reduced pressure. These higher bases form but a small fraction of the entire product, of which pyridine and lutidine constitute about 40 per cent., picoline and collidine being present in smaller proportion. The first three bases of the series, freed from foreign substances by treatment with oxidising agents, and purified by fractional distillation, gave the following results:—

|                | B. p.         | Density at $0^{\circ}$ . |
|----------------|---------------|--------------------------|
| Pyridine ..... | $115^{\circ}$ | 0.9802                   |
| Picoline.....  | 135           | 0.9660                   |
| Lutidine ..... | $156.5$       | 0.9377                   |

The density therefore diminishes as the molecular weight increases, a result in accordance with Anderson's observations, but not agreeing with those of Thenius. Some difficulty was experienced in purifying collidine. The fraction boiling at  $176$ — $180^{\circ}$  was treated several times in succession with strong nitric acid, but the residue was still considerably acted on by that acid. Fuming nitric acid converts this base into a product which explodes on concussion. The best agent for the purification of collidine appears to be chromic acid, the base being dissolved in sulphuric acid. After four purifications by chromic acid the base was obtained as a colourless liquid, becoming slightly tinted by action of the air: b. p.  $179$ — $180^{\circ}$ ; density at  $0^{\circ}$  0.9291.

The platinochloride was obtained as a viscons, uncrystallisable, yellow-brown precipitate, insoluble in water and acids, from which the author could not succeed in regenerating the base. Collidine platinochloride is described by Anderson as a salt crystallising in prisms. On comparing the collidine purified as above with (1) the *aldehydine* of Baeyer, (2) the base obtained by Wurtz in distilling aldol-ammonia, and (3) the base  $C_8H_{11}N$  obtained by Greville Williams from the products of the distillation of cinchonine with potash, the

following differences were observed:—Aldehydine, prepared according to Baeyer's directions, is a colourless liquid boiling at  $179^{\circ}$ . Its platinochloride is identical with that of Wurtz's base, and is much more soluble in water than the platinochloride of the base from cinchonine. One c.c. of water at  $60^{\circ}$  dissolves 0.0213 gram of the platinochloride of the base from cinchonine, 0.0495 of the platinochloride of the base from aldol-ammonia, and 0.500 gram of the platinochloride of Baeyer's aldehydine. Analysis of Baeyer's aldehydine gave C 79.24 per cent. and H 9.90 per cent., and of the base from cinchonine C 79.00 per cent. and H 9.19 per cent. The author concludes that the collidine obtained by him from Dippel's oil is not identical with either of the above bases having the same formula. Dippel's oil contains a small quantity of ethyl alcohol. J. M. H. M.

**Alkaloids of the Pomegranate.** By C. TANRET (*Compt. rend.*, 90, 695—698).—The bark of the pomegranate tree contains four alkaloids:—

(1.) *Methylpelletierine*,  $C_8H_{17}NO$ , a liquid boiling at  $215^{\circ}$ , and forming very deliquescent salts. It dissolves in 25 times its own weight of water at  $12^{\circ}$ , and is very soluble in alcohol, ether, and chloroform. The hydrochloride has a rotatory power for  $[\alpha]_D$  of  $+22^{\circ}$ .

(2.) *Pseudopelletierine*,  $C_8H_{15}NO$ , a crystalline solid.

(3.) *Pelletierine*,  $C_8H_{15}NO$ , a colourless liquid, boiling at  $195^{\circ}$  under ordinary pressure, with partial decomposition, but may be distilled unchanged under reduced pressure. It dissolves in 20 times its own weight of water, and is soluble in all proportions in alcohol, ether, and chloroform; its sp. gr. at  $0^{\circ}$  is 0.988. When exposed to oxygen, it is rapidly converted into a resinous mass. The salts of this alkaloid become acid when heated either in the dry state or in solution. The sulphate has a rotatory power for  $\alpha_D$  of  $-30^{\circ}$ . If the free alkaloid be heated to  $100^{\circ}$ , this rotatory power disappears.

(4.) *Iso-pelletierine*,  $C_8H_{15}NO$ , a liquid without action on polarised light. Its specific gravity, solubility, and boiling point are the same as those of pelletierine, of which it is an isomeride. C. H. B.

**Daturine.** By E. SCHMIDT (*Ber.*, 13, 370—373).—According to Planta (*Annalen*, 74, 252) atropine and daturine are identical, whilst, according to Poehl (*Chem. Centr.*, 1878, 108), they are not. The author has carefully compared samples of daturine and atropine from various sources, and so far has been unable to detect any difference between the two. This conclusion is based on the following facts:—

The melting points of several samples of atropine varied from  $112.5^{\circ}$  to  $115.5^{\circ}$  ( $115.5^{\circ}$ , Ladenburg), and those of several samples of daturine  $113.5^{\circ}$  to  $115.5^{\circ}$ . Both gave the same results on analysis, viz.,  $C_{17}H_{23}NO_3$ , and both are slightly levorotatory, although Poehl states that atropine is inactive towards polarised light, whilst Bnignet (*Jahresb.*, 1861, 49) agrees with the author. The platinochlorides of the two bodies have both the composition  $(C_{17}H_{23}NO_3.HCl).PtCl_4$ , and the same melting point ( $208^{\circ}$ ). The gold salts also are to all appearance identical, and have the composition  $C_{17}H_{23}NO_3.HCl.AuCl_4$ . Both bases behave

in a manner exactly similar towards all ordinary reagents, and on boiling with baryta-water both yield atropine acid,  $C_8H_7O_2$  (m. p.  $106.5^\circ$ ), and tropine (m. p.  $63^\circ$ ; Kraut gives  $61.2^\circ$  as the melting point of tropine from atropine), the platino- and auro-chlorides of the latter base were also found to be identical, the composition of the platinochlorides being  $(C_8H_7NO.HCl)_2.PCl_4$ , and m. p.  $199^\circ$  with decomposition, and that of the auro-chlorides,  $C_8H_7NO.HCl.AuCl_3$ ,  $211^\circ$ .  
T. C.

**Daturine.** By A. LADENBURG and G. MEYER (*Ber.*, 13, 380—381).—Daturine is not identical with atropine, as stated by Planta (*Annalen*, 74, 252), but with hyoscyamine and duboisine. This conclusion is based on a comparison of the respective melting points of the free bases (atropine =  $113.5^\circ$ , daturine =  $105$ — $108^\circ$ , hyoscyamine =  $108.5^\circ$ ), and on the properties and composition of the auro-chlorides, the melting points of the hyoscyamine and daturine compounds being identical, viz., =  $159^\circ$ . Daturine and hyoscyamine also behave in an exactly similar manner towards reagents.  
T. C.

**Synthesis of Ulmic Substances.** By A. MILLOT (*Compt. rend.*, 90, 611—612).—When a 5 per cent. solution of ammonia is electrolysed, the negative pole being of platinum and the positive pole of purified gas carbon, the carbon becomes disintegrated and a black liquid is obtained; the addition of a mineral acid to this produces a precipitate which, when purified by solution in water and reprecipitation, has the composition C 54.75, H 4.00, N 12.40, O 28.85. It is entirely soluble in water, especially if warm, but is insoluble in alcohol, which precipitates it from its solutions. When dried it becomes partially insoluble in water, but dissolves completely in solutions of ammonia. After drying at  $150^\circ$  it is altogether insoluble in water. When boiled with alkali it does not evolve ammonia. Heated with potash it gives potassium cyanide.

By substituting potash or soda for ammonia, substances are obtained which have similar properties, but contain no nitrogen.

C. H. B.

**Gluten.** By T. WEYL and BISCHOFF (*Ber.*, 13, 367—369).—The gluten which is obtained by the action of water on flour does not exist ready formed in the latter, but is due to the action of some ferment on the vegetable myosin present in the flour. This ferment, however, has not yet been isolated.  
T. C.

**Products of the Decomposition of Proteids.** By BLEUNARD (*Compt. rend.*, 90, 612—614).—The mixture having the general formula  $C_nH_{2n}N_2O_4$ , obtained by the action of baryta on stag's horn, consists mainly of a glucoprotein of the composition  $C_6H_{12}N_2O_4$ , corresponding with the compound  $C_7H_{14}N_2O_4$ , obtained by Schützenberger from albumin. When treated with bromine, it is converted into a substance,  $C_6H_{12}N_2O_4$ , which is a mixture of glycocine,  $C_2H_5NO_2$ , and a compound,  $C_4H_7NO_2$ , in equivalent proportions. A body such as  $C_6H_{12}N_2O_4$  may be regarded as a molecular combination of  $C_2H_5NO_2$ ,

with a luceïne,  $C_4H_7NO_2$ , which on oxidation is converted into  $C_4H_7NO_3$ . The reaction with bromine may serve as a means of determining the constitution of gluco-proteins. C. H. B.

**Chemical Composition of Aleurone Grains.** By S. H. VINES (*Proc. Roy. Soc.*, 28, 218).—When the ground seeds of the blue lupin (*Lupinus varius*) are treated with a 10 per cent. solution of common salt, a fluid is obtained which gives the characteristic reactions of globulin. From this liquid water precipitates vitellin, and excess of common salt precipitates myosin.

The author concludes from an experiment, which is not very clearly explained, that conglutin is a product of the alteration of the reserve-proteids (globulins) and does not pre-exist in the seed.

In addition to vitellin and myosin there is another substance present in the 10 per cent. sodium chloride solution, which is not precipitated either on boiling or by addition of water or of salt. It is extracted from the seeds by boiling water. Its reactions indicate that it is allied to the peptones, most nearly resembling Meisner's  $\alpha$ -peptone (hemialbumose, Kuhne). It is precipitated from its aqueous solution by alcohol, but retains its solubility in water even after keeping in alcohol for three months. C. W. W.

## Physiological Chemistry.

**Specific Heat of Animal Tissues.** By I. ROSENTHAL (*Bied. Centr.*, 1879, 633).

|                              | Specific heat. |
|------------------------------|----------------|
| Compact bone substance ..... | 0.300          |
| Spongy " " .....             | 0.710          |
| Fatty tissues .....          | 0.712          |
| Striated muscle .....        | 0.825          |
| Defibrinated blood .....     | 0.927          |

Dried muscle gave 0.30 specific heat, and calculating the active muscle as consisting of three parts water and one part organic substance, the specific heat would be 0.825, a result which exactly corresponds with the experimental number.

The influence of water on the specific heat of a substance is shown by the approximation of its specific heat to that of water. The above determinations were made with Bunsen's ice-calorimeter at an initial point of  $40^\circ$ , and can be regarded as only approximate on account of the difficulty in fixing the initial temperature. A. J. C.

**The Function of Respiration at Various Altitudes on the Island and Peak of Teneriffe.** By W. MAROET (*Proc. Roy. Soc.*, 28, 498).—The experiments were performed by the author on himself and his guide at three stations, respectively 7,090, 10,700, and 12,200 feet above the sea-level. The functions investigated were the number

of respirations, the volume of air, amount of carbonic acid and amount of water expired per minute at the three stations, both while at rest and while doing a definite amount of work. By the comparison of the results with those obtained in a previous series of experiments on the Alps, the effects of increased temperature were determined.

The results obtained may be summarised as follows:—

The carbonic acid expired is, under all circumstances, proportional to the weight of the body; for the subjects of these experiments it was 676 mgrms. per 100 kilos. The amount was greatest during the first or second hour after eating, afterwards gradually diminishing.

The amount of carbonic acid expired was greater at Teneriffe than on the Alps, the increase amounting to 14.0 and 17.5 per cent. for the author and his guide respectively. There was no increase in one case at the greater elevations such as was experienced on the Alps, the increase in the latter case being probably due to reduced temperature. In the other case, however, 17 per cent. more carbonic acid was expired at the sea-level than on the Peak of Teneriffe. This was due to increased perspiration at the higher altitudes.

The volume of air expired per minute, and also the number of respirations decreased at the higher elevations. The percentage of carbonic acid in the air expired increased from 4.1 per cent. at the sea-level to 4.9 per cent. at 11,945 feet.

With respect to the effect of work, it was found that the relation between the *volumes* of air expired while sitting and while engaged on a regulated amount of muscular work, was the same as the relation between the *weights* of carbonic acid expired under such circumstances.

The amount of water expired increases considerably from the lower to the higher level; this causes a very great loss of heat at the higher elevation.

C. W. W.

**Digestion of Albuminoids.** By A. SCHMIDT (*Bied. Centr.*, 1879, 887—890).—Six dogs of the same breed, after two days' fasting, were fed each with 200 grams of flesh and killed with potassium cyanide at various intervals after the meal. The stomach and intestines were then examined. It was found that, after a lapse of more than nine hours, some of the food still remained undigested in the stomach. As regards the digestion of the albumin, it was observed that a constant quantity of dissolved albumin remained in the stomach during the digestive process, and the peptone varied from one and a half to twice the amount of dissolved albumin. The food passed through the dogs in about nine hours.

J. K. C.

**Digestion in Sheep.** By E. v. WOLFF and others (*Bied. Centr.*, 1879, 890—901).—The object of these researches was to ascertain the influence which the addition of bye-fodder, such as potatoes and beet-root, has on the digestion of ordinary raw fodder, hay, straw, and the like. For two months beet was given to two sheep along with clover hay: the composition of each was as follows:—

|                    | Protein. | Fat. | Fibre. | Nitrogen<br>free extract. | Ash. |
|--------------------|----------|------|--------|---------------------------|------|
| Clover hay . . . . | 19.37    | 3.84 | 24.45  | 43.92                     | 8.42 |
| Beet. . . . .      | 13.60    | 0.56 | 7.04   | 70.35                     | 8.45 |

The plan of the experiment and the results as mean of both animals, are appended in the following table:—

| Fodder per diem.             |                   |                 | Percentage of clover hay digested. |                    |          |       |        | Nitrogen<br>free<br>extract. |
|------------------------------|-------------------|-----------------|------------------------------------|--------------------|----------|-------|--------|------------------------------|
| Period.                      | Clover.<br>grams. | Beet.<br>grams. | Solids.                            | Organic<br>matter. | Protein. | Fat.  | Fibre. |                              |
| I..                          | 1000              | —               | 57.76                              | 59.53              | 60.28    | 55.01 | 55.25  | 63.43                        |
| II..                         | 1000              | 2000            | 54.02                              | 55.62              | 54.68    | 50.62 | 45.69  | 61.82                        |
| III..                        | 500               | 2000            | 53.94                              | 56.10              | 53.16    | 39.90 | 48.11  | 62.90                        |
| Percentage of beet digested. |                   |                 |                                    |                    |          |       |        |                              |
| II..                         | —                 | —               | 85.78                              | 85.00              | 71.35    | —     | —      | 96.19                        |
| III..                        | —                 | —               | 85.92                              | 86.53              | 71.59    | —     | —      | 96.17                        |

Similar experiments with potatoes as bye-fodder showed that in this case also a lowering of the digestive coefficient of the hay took place, the percentage of total solids digested being reduced from 60.2 to 47.3, and of protein from 63.7 to 45.9. In other experiments, the clover was replaced by hay and pasture grass, and the potatoes by sugar beet, turnips, and swedes. In all cases a lowering of the digestive coefficient of the raw fodder resulted, varying in each case according to the absolute amount of each constituent present in the bye-fodder.

J. K. C. .

**Nutritive Value of Asparagine.** By H. WEISKE, M. SCHRODT, and ST. V. DANGEL (*Zeits. f. Biologie*, 15, 261—296).—Various experimenters have found that amido-compounds, as glycocine, leucine, tyrosine, asparagine, and aspartic acid, are converted into urea in the animal system. Knieriem also found that when asparagine was given to a dog receiving an insufficient diet, it diminished the previous loss of albumin in the body. Gelatin has been shown by Voit and others to discharge the same function. As amides are generally present in succulent and immature vegetable food, the authors made the following experiments to ascertain their value in the animal economy.

Four rabbits were fed on a mixture of 50 grams starch, 10 grams oil, and 2 grams vegetable ashes. To this mixture was added in one case 5 grams asparagine, in another case 10 grams gelatin, and in a third case 5 grams of both asparagine and gelatin. The rabbit receiving gelatin died on the 38th day, but without any serious loss in weight. The rabbit receiving no nitrogenous food died on the 49th day, having diminished in weight from 1125 to 640 grams. The rabbit with the asparagine ration died on the 63rd day, after a gradual diminution in weight, which became rapid towards the close. The fourth rabbit, receiving both asparagine and gelatin, increased in weight, and was alive on the 72nd day, when the experiment closed. Asparagine thus merely somewhat retarded death, while asparagine



mixed with gelatin was apparently capable of forming albumin in the animal body, and thus permanently sustaining life. A mixture of tyrosin and gelatin has been similarly found by Escher to be capable of replacing albumin.

Experiments were next made with hens, the diets employed being similar to those just described. The hens did not consume enough food to maintain their body weight, those receiving asparagine and gelatin were however quite healthy at the end of 17 days. With gelatin as the only nitrogenous food there was less success.

The final experiments were made on sheep. Two full-grown sheep received in the first experimental period 500 grams hay, 200 grams starch, and 50 grams sugar per head per day. In three succeeding periods the nitrogen in the diet was doubled by the respective addition of albuminoids, asparagine, and gelatin. Towards the end of each period, the solid excrement and urine were collected and analysed. It appeared that the asparagine was perfectly digested, the albumin (supplied as pea-meal) was also almost completely taken up, while the gelatin was less perfectly assimilated. By comparing the quantity of nitrogen and sulphur supplied in the food with that voided in the excrements, the amount retained as albuminoids in the body was calculated. On the first diet, the average amount of nitrogen retained by the sheep was 0.275 gram, and of sulphur 0.029 gram per day. With gelatin, the nitrogen retained amounted to 1.330 gram, and the sulphur to 0.038 gram. With asparagine, the nitrogen retained was 1.664 gram, and the sulphur 0.112 gram. With albumin, the nitrogen retained was 2.048 grams, and the sulphur 0.176 gram. It appeared, therefore, that the supply of both asparagine and gelatin increased the amount of albumin stored up in the body. The authors believe that asparagine and gelatin protect albuminoids from oxidation in the animal economy, and thus allow albumin to be stored up even under a poor diet.

R. W.

**Physiology of Sugar in Relation to the Blood.** By F. W. PAVY (*Proc. Roy. Soc.*, 28, 520).—After a comparison of the results obtained by various processes for the estimation of sugar in blood, in which he gives the preference to the ammoniacal cupric test, the author examines Bernard's hypothesis that the natural seat of destruction of sugar in the system is in the systemic capillaries. If this is the case, then a disappearance of sugar should occur in the blood after removal from the vessels; and, according to Bernard, such a disappearance does actually take place. The results obtained by the author, however, directly contradict those of Bernard, and point to the conclusion that the gradual disappearance of sugar which takes place in putrefying blood is the result of ordinary decomposition, and does not arise from any physiological cause.

The author also concludes, from the results he has obtained, that there is in the blood a reducing substance besides sugar, which is of a sufficiently stable character to resist advanced decomposition.

C. W. W.

**Muscular Activity and Waste.** By O. KELLNER (*Biol. Centr.*, 1890, 24—27).—A record of observations on a horse, regularly fed

and worked, in order to throw some light on the question whether muscular activity is caused simply by the oxidation of non-nitrogenous substances in the body or by the increase of albuminous matters in the food, as held by two schools of physiologists. The horse was periodically carefully weighed, his work estimated by a specially invented dynamometer, his consumption of food and water recorded, and his urine carefully collected and tested for nitrogen. The general results of the experiments show that with an increase of work, changes of albuminoid matters become more active. An increase of water drunk by the animal causes an increase in the evacuation of albuminoids.

The author draws an inference from the present and his former observations, that the source of muscular strength in general is the waste of organic matter. In the first place, the non-nitrogenous substances, hydrocarbons and fats, are called into requisition, the organic albuminoids not being attacked until the other materials capable of oxidation are no longer present in sufficient quantity. J. F.

**Observations on the Milk of a Large Herd of Cows.** By W. FLEISCHMANN and P. VIETH (*Bied. Centr.*, 1879, 908—911. The mean results of a year's examination of the milk of several cows are given in the following table:—

|                            | Morning milk. | Evening milk. |
|----------------------------|---------------|---------------|
| Specific gravity.....      | 1.0316        | 1.0318        |
| Percentage of fat .....    | 3.374         | 3.420         |
| Yield per cow in kilograms | 3.552         | 3.439         |
| Yield of fat in grams .... | 120           | 116           |

The percentage amount of fat varied from 2.844 to 3.927 per cent.

J. K. C.

**Influence of Ground Nuts on the Production of Milk.** By W. J. KIRCHNER and P. DU ROI (*Bied. Centr.*, 1879, 903—906).—Ground nut cakes, containing 52 per cent. of protein, gave favourable results as regards the production of milk, but seemed to have no special effect on the quantity of fat produced. J. K. C.

**Influence of Shearing on Yield of Milk.** By H. WEISKE (*Bied. Centr.*, 1880, 31, 32).—Previous observations convinced the author that the effect of shearing was to cause a greater appetite, but not a better digestion of the fodder. The removal of the hair necessitates a greater internal warmth in the body, which must be sustained by digested food; consequently, fodder, which should go to increase the production of flesh, is expended in producing heat, so that a diminution in the amount of flesh formed takes place.

The frequent shearing of fattening sheep is, therefore, not profitable, except for the purpose of increasing the animal's appetite and consumption of food, in order to indirectly increase the production.

The present observations were made upon a 2½ year old Southdown ewe, which lambed on 22nd April, unshorn, milked carefully three times daily, receiving regularly each day 1 kilo. of turnips, ½ kilo. of hay, and ½ kilo. of groats; she yielded on each consecutive—

|          |     |     |     |     |     |     |     |     |           |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----------|
| Day .... | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9         |
| Grams .. | 523 | 620 | 736 | 768 | 840 | 910 | 924 | 992 | 987 milk. |

From 10—20th of May the daily yield was very regularly 1,000 grams. On the 21st of May the ewe was shorn, the same food and treatment was continued, and a decided falling off was evident.

|              |      |     |     |     |     |     |
|--------------|------|-----|-----|-----|-----|-----|
| Date, May .. | 20   | 21  | 22  | 23  | 24  | 25  |
| Grams .....  | 1006 | 913 | 854 | 781 | 750 | 712 |

On the 26th of May  $\frac{1}{2}$  kilo. of linseed cake was added to the other food, with very beneficial results.

|             |     |     |     |     |     |     |
|-------------|-----|-----|-----|-----|-----|-----|
| May .....   | 26  | 27  | 28  | 29  | 30  | 31  |
| Grams ..... | 687 | 760 | 889 | 950 | 910 | 961 |

The yield of milk evidently suffered from shearing, and the addition of the linseed cake brought it up to its normal amount.

It appears reasonable from this that when the lambing season coincides with the time of shearing, the ewes should be generously fed with artificial food, unless they have the run of a good meadow, where they have food *ad libitum*. J. F.

**Influence of Impure Water on Health.** By R. EMMERICH (*Bied. Centr.*, 1880, 4—12).—A belief that such diseases as typhus and cholera are propagated by means of impure water is prevalent not only amongst medical men, but the general public, and exercises an important influence on the expenditure of town corporations and similar bodies in the endeavour to supply the pure and remove the impure water. The author of the present paper, believing from the experiments of Pettenkofer and others that this deleterious influence either does not exist at all, or if at all, in the most trifling degree, undertook the experiments recorded on the bodies of animals and his own person in order to contribute to the settlement of the question.

The experiments on animals consisted of subcutaneous injections of distilled, ordinary, and impure waters. The first experiments showed that with rabbits weighing from 760 to 1,500 grams, the injection of 40—70 c.c. of distilled water produced no observable alteration in their health, and that it required a considerable quantity, fully 200 c.c., to kill them. With impure water different results were obtained. The water selected was from the drain which collects the sewage of part of Munich, and discharges it into a brook; the temperature before injection was kept at blood heat, and the results were uniform, viz., that with animals weighing 550 to 1,500 grams, quantities of 6 to 60 c.c. invariably caused death in shorter or longer periods, the symptoms differing only according to the amount of the dose and the weight of the animal operated on; the temperature of the body rose in each experiment, but the author hesitates to ascribe that effect to the oxidation of the impurities of the water. With *boiled* sewage water the results were very similar to those with clean water, 14—24 c.c. producing but slight sickness, quickly recovered from, and death taking place only after injection of comparatively large quantities, say 150 c.c. Two other experiments were made with the residue of evaporated

sewage water; 500 c.c. evaporated on the water-bath and dissolved in a small quantity of distilled water; the injection of this matter produced strong convulsions and speedy death. The net result of this first series of experiments shows that the subcutaneous injection of impure water causes symptoms quite analogous to those produced by putrid fluids, and that its effects are the more intense the greater the quantity of oxidisable impurity contained in the water.

These experiments do not show whether the poisonous matter is in solution or suspension, or whether or not it is an organised ferment; but the author inclines to the opinion that it is *not* an organism, and that the similarity of the behaviour of the boiled sewage and its extracted residue with other preparations of putrid solutions leads him to the belief that the poisonous qualities are due to putrefactive matter in the sewage.

The author next directed his attention to the introduction of impure water into the stomachs of animals, and the results agree very closely with other experiments made with putrid poisons, viz., that a much larger quantity can be introduced into the stomach than either into the veins or under the skin. In the present case a rabbit weighing 1,500 grams received daily 600 c.c. of sewage water in four doses of 150 c.c. At the end of two days the animal appeared unharmed.

The author thinks it would be unsafe to say that the effects on human beings would be the same as on animals, and if the poison be an alkaloid or anything of that nature—say, similar to morphine—its toxical effects would vary very considerably; and taking into account the slight effect of large doses on such small animals as rabbits, he is of opinion that human beings could with impunity partake daily of a considerable quantity of sewage water. To test the matter, he determined to drink daily one-half to one whole liter of water taken from one of the small brooks or water-courses of Munich, which received the drainage from kitchens, wash-houses, urinals, cattle-sheds, &c., moreover, there were cases of typhoid in some of the houses draining into it; on the surface floated cabbage and lettuce leaves, human and animal hair, &c. He continued the experiment “a long time,” not exactly defined, but without feeling any injurious effects. A slight stomach cough with which he was affected at the beginning of the observations did not become any worse; and he inclines to the opinion that the unpleasant effects experienced by other people may have arisen from feelings of nausea at the appearance of the water. The author invites other investigators to continue similar experiments.

Injections of largely diluted sewage yield negative results, and the author agrees with Nägeli that the addition of large quantities of water to sewage renders the poisonous matter innocuous.

The author proposes a rough method of estimating the evil effects of impure water, which is, that the suspected water or its residue dissolved in 40 to 80 c.c. be injected under the skin of a full-grown rabbit; if the increase of temperature is no greater than  $1^{\circ}$  C., or if death do not follow in a very short time, there is no harmful matter present, or it is present in trifling quantity.

He has examined the worst of the Munich waters by this method and thinks it fairly trustworthy, but that it, in common with all known

processes for estimating organic impurities in water, must be considered as temporary expedients to give way to some method yet to be devised.

J. F.

**Presence of Copper in Food.** By A. GAUTHIER (*Bied. Centr.*, 1879, 937—938).—Experiments on dogs showed that doses of some decigrams of copper sulphate could be given daily without producing death, but further researches are necessary to ascertain whether permanent derangement of health is not produced. It was found that wheat, coffee, starch, &c., contain about 1 mgrm. of copper per kilo.

J. K. C.

**Injury to Fishes by Waste Liquids.** By WEIGELT (*Landw. Versuchs.-Stat.*, 24, 424—427).—Trout weighing 5—20 grams die in a few minutes in water containing 0.005 gram chlorine per liter, and even 0.0002 gram per liter is undoubtedly fatal to small fish; and this is near the limit of the amount of chlorine that can be detected by chemical means. Soda-lye, and even ammonium carbonate, act much less injuriously; fish kept in solution of soda containing 3 grams and 0.1 gram of crystallised soda per liter for 15 and 45 minutes respectively seemed to be uninjured; at least they were living six weeks afterwards in a running stream. Sulphuric acid was more fatal by far than hydrochloric acid, but the fish soon recover themselves when removed from the contaminated water. Waters charged with carbonic anhydride, neutral salts (calcium chloride and sodium chloride), with a concentration of 3 parts per 1,000, have no injurious influence.

J. T.

**Cobra Poison.** By A. PEDLER (*Proc. Roy. Soc.*, 27, 17), A. W. BLYTH (*Analyst*, 1, 204), and T. L. BRUNTON and SIR J. FAYRER (*Proc. Roy. Soc.*, 27, 188).—The poison of the Cobra de Capello (*Naja tripidians*), which may be obtained by pressing the parotid glands of the snake while its fangs are erected, is an amber-coloured, syrupy, frothy liquid, of sp. gr. 1.046 (Blyth), 1.095 at 23° (Pedler). When evaporated, either in the air or in a vacuum, or at 100°, it leaves a solid residue amounting on the average to 28.82 per cent. (Pedler); about 33 per cent. (Blyth). The fresh liquid has no action on polarised light. It may be kept for two or three months without alteration, but after a year or 18 months it alters considerably, becoming insoluble, and losing to a great extent its poisonous action (Pedler).

Dried in a vacuum over sulphuric acid, it gave by analysis:—

| C.    | H.   | N.    | Ash. | O with<br>trace of S. |
|-------|------|-------|------|-----------------------|
| 49.32 | 7.01 | 17.89 | 6.68 | 19.60 = 100           |

or deducting the ash:—

| C.    | H.   | N.    | O and S.    |
|-------|------|-------|-------------|
| 52.87 | 7.51 | 18.29 | 21.33 = 100 |

This composition does not differ greatly from that of various kinds of albumin; the proportion of nitrogen, however, is rather greater than in egg-albumin.

The liquid poison, treated with strong alcohol, yielded a precipitate

of albuminous matter, amounting to about 17·3 per cent. of the whole, which was only slightly poisonous, whereas the portion soluble in alcohol (10·9 per cent. of the whole) was excessively poisonous: hence, as the total quantity of solid matter in the poison is about 28 per cent., it follows that about 60 per cent. of the poisonous liquid is of an albuminous nature, and only about 40 per cent. consists of pure poison. No crystallisable substance could be obtained from the poison, either by the use of solvents or by dialysis through parchment paper, although slight indications of crystallisation were obtained by both methods. The liquid remaining in the dialyser left on evaporation a gummy mass, having all the physiological characters of the poison; and the liquid outside the dialyser appeared to be rather more poisonous than the original virus (Pedler).

According to Blyth, cobra poison contains albumin, and a minute quantity of fat, and yields about 1·4—1·5 per cent. of ash, mainly consisting of sodium chloride. It dries up quickly on exposure to the air, leaving a yellow acrid pungent powder, amounting to about 33 per cent. of the whole. This substance is not decomposed at 100°, but blackens at 270°, and yields a sublimate at higher temperatures. A similar substance, crystallising in needles, may be obtained by dialysing the poison. It exists therein to the amount of 10 per cent., and is highly poisonous, appearing to be the only active principle. It is obtained pure by conversion into a lead-salt, separation therefrom, and evaporation in a vacuum. Blyth designates this substance as *cobric acid*. He finds that a weak solution of potash, or a weak alkaline solution of potassium permanganate, destroys the physiological activity of cobra poison.

Pedler describes a long series of experiments on the modification of the active properties of the poison by various substances, undertaken with the view of discovering an antidote to its action. When the poison was digested with *ethyl iodide*, a residue was obtained which exhibited an increase of weight, indicating combination, and was much less active than the original poison. The residue obtained by mixing the poison with hydrochloric acid and leaving the liquid to evaporate, was also much less active than the original poison. By slow evaporation in a vacuum, distinct traces of crystals were obtained, but they were mixed with a large quantity of amorphous soluble matter, from which they could not be separated.

A much greater diminution of the activity of the poison is produced by the addition of *platinic chloride*. When a quantity of fresh cobra poison was treated with alcohol to precipitate the albumin, the alcoholic filtrate acidified with hydrochloric acid, and a solution of platinic chloride added, a small quantity of a yellow amorphous precipitate was formed, and the solution evaporated in a vacuum yielded a semicrystalline residue, which was freed from excess of platinic chloride by washing with weak spirit. 0·1 gram of the solid platinum compound administered internally to a chicken exerted no poisonous action, and the solution containing the excess of platinic chloride was likewise without action when injected hypodermically. A considerable number of experiments upon chickens and dogs showed that even considerable quantities of cobra poison mixed with platinic chloride

might be injected hypodermically without producing a fatal result, provided a short time was allowed to elapse before the mixture was injected. In one experiment, the quantity of poison thus injected was sufficient, if administered alone, to kill 120 chickens. When, on the other hand, the injection was performed immediately after mixing, the results were less favourable, the fatal effect being not prevented, but merely retarded. The same effect of retardation, but not prevention of the fatal result, was obtained when the cobra poison was first injected alone, and the platinum solution a few minutes (1 to 5) afterwards. The poison indeed seems to diffuse itself through the organism so rapidly that no antidote can be afterwards injected quickly enough to counteract its effects.

The platinum salt of the cobra poison gave by analysis numbers nearly agreeing with the formula,  $(C_{17}H_{25}N_4O_7.HCl)_2.PtCl_4$  (Pedler).

Branton and Fayer find that auric chloride behaves similarly to platinic chloride, rendering the poison nearly inactive if mixed with it before injection. Permanganate of potassium also prevents the fatal effect, probably by destroying the poison. Zinc chloride, mercuric chloride, silver nitrate, and carbolic acid also diminish the activity of the poison, and slightly prolong life if mixed with it before injection. Ferric chloride has a weaker action. Potash prolongs life for several hours. With large doses of the poison, none of these substances have any appreciable effect, even when applied immediately.

C. W. W.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Locality of Albumin Secretion in Plants.** By H. MÜLLER THURGAU (*Bied. Centr.*, 1880, 42—43).—The author endeavours to decide whether the formation of *protoplasm* takes place in the leaves or other portions of the plant; for this purpose he devises an arrangement by which the seeds of maize, wheat, beans, &c., are germinated over water, and the rootlets led out in two divisions, and immersed in separate vessels; the two vessels contain solutions which are identical as regards mineral constituents, but to one of them is added a nitrogenous substance of easy assimilation, the other contains *nons*. The growth of the rootlets was measured regularly every day.

If the development of the albuminoid was due to absorption from the air, or had its origin in the upper portions of the plant, both divisions of the root should grow equally. If, however, it proceeded from the roots, the portion immersed in the solution containing nitrogenous matter should grow quicker than the other; this was actually the case. The leaves do not appear to play any part in the assimilation. To prevent mistakes, the roots were alternately immersed in one solution, and changed to the other; their growth varied exactly and daily as they were placed in one or other solution. The same results were obtained from placing the rootlets in sand saturated with a nitrogenous solution.

The practical application of these experiments shows that there is advantage in the use of a nitrogenous manure in cases where quick and strong development is desirable, as for example in turnip and tree culture.

J. F.

**Decomposition of Albuminoids in Plants.** By E. SCHULZE (*Bied. Centr.*, 1879, 609—610).—The author advances the theory of the alternate decomposition and re-formation of albuminoids in the organism of plants, and to this end he discusses the production in the lupine of asparagine from conglutine.

A. J. C.

**Passage of Nutritive Material in Plants.** By L. DESBARRÈS (*Bied. Centr.*, 1879, 946—947).—The wood of young branches of *Rhus elegans* was examined in winter and spring with the following results:—

|                    | In winter. | In spring. |
|--------------------|------------|------------|
| Dry substance .... | 72.16      | 66.70      |
| Protein .....      | 9.42       | 2.25       |
| Starch .....       | 17.31      | 1.57       |
| Ash.....           | 1.60       | 1.20       |

The woody parts of the plant seem, therefore, in winter to form a reservoir for assimilable material for the nourishment of the young organs in spring.

J. K. C.

**Amount of Dew on Plants.** By L. HANPEL (*Bied. Centr.*, 1879, 630).—The observations were made in July and August.

|   | With dew.   | Without dew. | Dew by difference. |
|---|-------------|--------------|--------------------|
|   | centigrams. | centigrams.  | centigrams.        |
| <i>Pinus austriaca</i> , four needles gave .... | 45.60       | 40.76        | 4.84               |
| <i>Tilia grandifolia</i> , one leaf gave.....   | 106.80      | 82.40        | 24.40              |
| <i>Tubercus pedunculata</i> , one leaf gave.... | 96.06       | 71.50        | 24.56              |
| <i>Abies excelsa</i> , a small bough gave.....  | 85.10       | 75.30        | 9.80               |

A. J. C.

**Fertilization of Rye.** By W. RIMPAU (*Bied. Centr.*, 1879, 911—912).—The author finds that the flowers on the same plant cannot fertilize each other, and that pollen from other individuals is necessary for this purpose.

J. K. C.

**Result of Drying Seeds.** By E. WOLLNY (*Bied. Centr.*, 1880, 36—42).—Many experiments have shown that the seeds of several plants including flax, cucumbers, pumpkins, and melons, yield very plentifully when they have been dried at a temperature of 30° to 50° C., notably flax seed, growers of which always seek old seed, as yielding a better and longer flax; the author presumes this is because of the natural drying of the moisture originally contained in the seeds. This fact led the author to undertake a series of experiments with the seeds



of many food plants in order to learn the effect of artificial drying on their productiveness.

In view of the danger of too high a temperature killing some of the seeds, they were not heated above  $32-35^{\circ}\text{C}$ , so that a long time was necessary to dry them; the undried seeds were meanwhile kept in airtight bottles, and lost scarcely any moisture. The experiments were arranged in two series, firstly, to ascertain the effect upon the *growth* of the plant, and, secondly, the effect upon the productiveness. The answer to the first question is that the drying of the seeds delays the growth of the plant, and that the plants produced from the dried are much more irregular in size than those from undried seeds, and that notwithstanding the greatest care in drying, the seeds so treated have a less percentage of germinating power. The effect on the crop, however, is very different, the figures showing clearly that the effective produce of the dried seeds is greater than from the undried.

The author confesses his inability to reconcile the different conclusions, but suggests that a great deal depends on the state of the soil, whether it contains abundance of natural moisture or not, and suggests that after all it is to a great extent dependent on the nature of the locality and the facilities for obtaining water, and hopes that practical farmers will carry out further experiments.

J. F.

**Normal Presence of Copper in the Plants which Grow on Primordial Rocks.** By DIEULAFAIT.—The author has previously shown that all rocks of primordial formation contain copper. He finds that this element is present in plants growing on such rocks to such an extent that it may be recognised by the ammonia reaction in 1 gram of ash. Copper is also present in the ashes of plants growing on marls, the sand of which has been derived from primordial rocks. Other researches have led the author to conclude that heat has had nothing to do with the formation of dolomites. They are marine formations, sedimentary in the ordinary sense of the word, but often deposited in concentrated marine waters. He has previously found that deposits found in such waters always contain copper, therefore dolomites ought to contain this element. Plants growing on dolomites contain copper to such an amount that it can be detected in 1 gram of ash. On the other hand, plants growing on pure limestones contain but traces of this metal, requiring at least 100 grams of ash for its detection.

C. H. B.

**Formation of Nitrates in Sugar Beets.** By A. PAGNOUL (*Bied. Centr.*, 1880, 17).—These salts when found are not always derived from mineral manures added to the soil, but may come from organic nitrogenous substances, such as stable manure. Beets which were sown in ground manured with sodium nitrate, although containing a considerable quantity of the salt immediately after germination, contained no trace at a later period, whilst some from the same seed, sown in ground which had been heavily manured with stable dung, contained 0.7 per cent. of the salt.

Very great care must be taken when cultivating beets to avoid every cause that might lead to late vegetation; the leaves should attain

their full development by the end of August; if a slowly working manure be employed, or the season be mild, dull, and damp, and the development is delayed until September or October, it is at the expense of the saccharine matter of the roots; they continue to grow, and take up salts from the soil which they have not vigour to assimilate.

When nitrates are found in the roots under such circumstances, allowance should be made for the season and the slow or quick nature of the manures employed. J. F.

**Nitrates in Sugar-Beets.** By J. A. BARRAL (*Bied. Centr.*, 1880, 44—45).—An English farmer sent to the French Agricultural Society in December, 1878, a number of large beets, some of them weighing 14 kilos. They were found poor in sugar and were employed for feeding purposes; they were analysed, and it was found that nitrates were most abundant in those which were poorest in sugar, the proportions being very constant. The sugar manufacturers have for a long time forbidden the use of nitrate of soda on the farms which supply them with roots, and the author's researches prove them to be right, the beets experimented on having been heavily manured with sodium nitrate. He also believes that the feeding of cattle largely with such roots would be attended with injurious consequences. In the following table the amounts of nitrogen, nitrates, and sugar are the percentages contained in the dry substance, the nitrates being calculated as nitric acid:—

| Name.                 | Weight of root, kilos. | Dry substance per cent. | Nitrogen per cent. | Nitric acid per cent. | Sugar. |
|-----------------------|------------------------|-------------------------|--------------------|-----------------------|--------|
| Mammoth .....         | 14.150                 | 5.81                    | 3.54               | 13.80                 | 17.21  |
| Berkshire .....       | 10.600                 | 7.95                    | 3.27               | 4.98                  | 23.16  |
| Ox-heart .....        | 11.390                 | 6.35                    | 3.44               | 9.21                  | 31.50  |
| Tankard .....         | 8.920                  | 7.88                    | 3.12               | 11.39                 | 12.92  |
| Yellow globe .....    | 2.082                  | 11.54                   | 1.51               | 1.37                  | 34.66  |
| Horn .....            | 1.782                  | 12.60                   | 1.40               | 0.64                  | 31.75  |
| Giant .....           | 2.411                  | 9.46                    | 1.75               | 0.68                  | 52.86  |
| White green top ..... | 3.124                  | 11.92                   | 1.11               | 0.13                  | 58.72  |
| White red top .....   | 0.730                  | 16.73                   | 0.97               | 0.09                  | 48.10  |
| Kohl Rabi .....       | 6.200                  | 9.56                    | 3.33               | 4.55                  | 20.92  |

J. F.

**Beetroot.** By P. WAGNER (*Bied. Centr.*, 1879, 947).—Sugar beetroot from various sources was examined; the percentage of sugar varied from 10—14. J. K. C.

**Researches on Beetroot.** By A. BAUDRIMONT (*Bied. Centr.*, 1879, 916).—On cutting open a beetroot, two series of concentric rings are observed, the one white and opaque, the other clear, transparent, and mostly coloured; in the former the sugar is chiefly aggregated, and in the latter the albumin. The author has endeavoured to promote the special growth of one or the other set of rings by the appli-

cation of suitable manures. The roots were grown on four plots of land; one of these was treated with water, the rest in order with solutions of bicarbonate of ammonia, bicarbonate of potash, and a mixture of these. It was observed that the roots which had been watered with bicarbonate of potash solution were very large and hard, and consisted chiefly of the sugar bearing rings; those which had received bicarbonate of ammonia were much softer, hollow in the centre, and the albuminous rings were more strongly developed; those treated with a mixture of both were not so hard, and showed clear albuminous rings, whilst those which had received water alone were the strongest, and showed both kinds of rings clearly. J. K. C.

**Composition of Ash of two kinds of Beet Seed.** By H. BODENBENDER and IHLEE (*Bied. Centr.*, 1879, 948).—In 100 parts of the seed were contained (1) 7·80 and (2) 7·67 parts as ash.

The percentage composition of the ash was as follows:—

|     | Na <sub>2</sub> O. | K <sub>2</sub> O. | CaO.  | MgO. | Fe <sub>2</sub> O <sub>3</sub> . | Cl.  | CO <sub>2</sub> . | SO <sub>3</sub> . | P <sub>2</sub> O <sub>5</sub> . | SiO <sub>2</sub> . |
|-----|--------------------|-------------------|-------|------|----------------------------------|------|-------------------|-------------------|---------------------------------|--------------------|
| (1) | 25·73              | 6·75              | 22·18 | 5·72 | 1·77                             | 1·07 | 15·39             | 4·46              | 2·56                            | 13·59              |
| (2) | 32·93              | 4·97              | 13·44 | 3·91 | 3·86                             | 4·19 | 22·54             | 2·50              | 6·47                            | 5·11               |

J. K. C.

**Effect of Acid Gases on Vegetation.** By R. HASENCLEVER (*Bied. Centr.*, 1880, 57—58).—The author has collected a number of analyses of leaves of trees from the neighbourhood of chemical works, and from districts where such manufactories are not carried on. The results are interesting; but consisting as they do of different kinds of plants do not afford sufficient grounds for comparison, the author recommends the analysis of healthy and unhealthy plants from the same neighbourhoods when complaints of damage from acid vapours are made, and also wishes that the rain and air of such districts could be compared with samples of the same from other localities. J. F.

**Injury to Vegetation caused by Acid Gases.** By J. SCHRÖDER (*Landw. Versuchs.-Stat.*, 24, 392—421).—The author is of opinion that Stöckhardt's view is correct, namely, that the injurious effect of smoke from smelting works, chemical works, and from coal fires, is mainly due to sulphurous anhydride and other acid gaseous products. Wood-smoke does not injure vegetation, and the less sulphur is present in bituminous and brown coals the less injurious it is. A very short exposure to acid gases produced perceptibly injurious effects on the leaves; an alcoholic extract of the leaves then shows the absorption-bands of acid chlorophyll. All plants thus damaged show a diminished transpiration, depending on the amount of acid and time of exposure.

Numerous experiments show that sulphurous anhydride acts most strongly in presence of light, warmth, and moisture, but darkness is more efficacious as a preservative than dryness. Sulphurous anhydride is strikingly worse than hydrochloric acid. Sulphuric acid is less injurious than an equivalent amount of sulphurous anhydride, so that oxidation of the sulphurous anhydride present in smoke by the action of air and moisture is favourable.

Plants growing in an atmosphere containing sulphurous anhydride or hydrochloric acid show an excess of sulphur or chlorine respectively. Thus a young fir-tree growing in the laboratory in presence of sulphurous anhydride gave in 100 parts of dry needles 0·721 of sulphuric acid, whilst a healthy young tree gave 0·240 part. Different plants do not suffer equally in presence of sulphurous anhydride. In the following list those least influenced are placed first:—Oak, maple, ash, alder, poplar, lime, birch, red beech; then we have needle-leaved trees, pine, fir. The list agrees with observations made in the neighbourhood of metallurgical works. The effect of hydrochloric acid is probably the same.

The amount of sulphur and chlorine in healthy plants may vary within tolerably wide limits; thus an alder grown under the water-culture system gave 0·75 per cent. of sulphuric acid, whilst another grown in the soil gave 0·19 per cent., both being healthy plants. The presence of gypsum and salt in the soil affects the results of analysis; so that healthy plants grown under similar conditions as to soil should be examined along with suspected plants. Two maps of the Upper Harte smelting district were shown. In one the district was coloured to show the damage done to trees as determined by inspection. One colour showed trees destroyed, or very seriously damaged, another tint showed the region of trees perceptibly injured, and a third the region in which the damage from smoke was somewhat questionable, whilst a fourth tint showed the uninjured districts. 150 samples of leaves were taken, and the sulphuric acid determined in them: those giving 0·5 per cent. and upwards were found to fall within a district marked out on the second map, those with from 0·5 to 0·3 occupied another region, 0·3 to 0·21 a third, and all below 0·21 formed a fourth region; on comparing the two maps they were found to agree very closely indeed. The samples were taken during a week of autumn in 1878, and were mainly of fir-needles. In the discussion following, M. Freytag reported similar results founded on nearly 20 years' observation, but he was of opinion that sulphuric and hydrochloric acids were more injurious than sulphurous anhydride.

J. T.

**Injurious Effect of Industrial Effluent Water and of Gases on Soils and Plants.** By J. KÖNIG (*Bied. Centr.*, 1879, 564—567).—The author shows the importance of ascertaining that the water used for irrigation is free from any constituent which has a prejudicial action on vegetation. Effluent water from a zinc blende mine contains an appreciable amount of zinc sulphate, formed by oxidation of the sulphide, and the result of irrigating a meadow for some years with a stream which received such effluent water was to cause a considerable decrease in the yearly produce. Moreover, certain parts of the meadow became almost barren. The soil of the meadow was found to contain 0·13—0·964 per cent. zinc oxide, whilst the grass and plants (beech and maple) gave 4·13—6·53 per cent. of ash and 0·037—0·156 per cent. zinc oxide, which is equal to 0·86—2·78 per cent. in the ash. The soil and the plants from the apparently sound part of the meadow contained no zinc oxide.

The ash of three specimens of the white "erzblume" which grew

in places in the meadow on which zinc-ore had been spilt gave respectively:—

|                           |       |       |       |
|---------------------------|-------|-------|-------|
| Ash in dried plant.....   | 13.29 | 12.75 | 9.29  |
| Zinc oxide in the plant.. | 1.49  | 2.68  | 1.46  |
| Zinc oxide in the ash ..  | 11.27 | 21.40 | 15.81 |

Waste water from dye works, wire drawers, and from pyrites washing has an injurious action on vegetation: the first-named contains a large quantity of sodium sulphate and organic colouring matter, and the two last much ferrous sulphate; the pyrites waste water probably also contains a small quantity of free sulphuric acid.

The destructive influence of sulphurous acid fumes on plant life, which is observable in the neighbourhood of chemical works, has been investigated by the author, who states that the leaves, needles, and young twigs of the trees are first affected, and that these injured parts contain about 11—50 per cent. of sulphuric acid in excess of the normal quantity, and a proportional increase in the amount of ash.

A. J. C.

**Grass Mowing.** By E. WOLLNY (*Bied. Centr.*, 1879, 617—619).—It is the custom of some agriculturists to discontinue mowing grass land during a continuance of dry weather, as they hold the opinion that the grass retains the moisture which would be removed by mowing, and the after crop would be endangered in consequence. This erroneous idea has no doubt arisen from the fact that the upper surface of grass-covered land is damper than that of the fallow land (16.08 per cent. moisture against 11.93 per cent. in the author's experiments); but this is the case at the surface only, for at a lower stratum, whence the plants replace the water which has evaporated from their upper organs there is less moisture (22.54 per cent.) than from a similar stratum (28.59 per cent.) in a fallow land. The conclusion which is drawn from several experiments of the moisture contained at different depths in grass land and in fallow land is, that the amount of moisture in all kinds of soil covered with vegetation, grass for example, is always less than that in the same soil which is not covered with vegetation. As it is the vegetation which dries up the soil, it necessarily follows that the retention of the moisture is assured to the soil if the mowing takes place under the above condition of weather.

A. J. C.

**Relation of the Grasses of Meadows and Pastures.** By SPEER (*Bied. Centr.*, 1879, 919—921).—The author gives an account of the various weeds, sour grasses, &c., occurring on meadow and pasture land.

J. K. C.

**Digestibility of Steamed Hay.** By U. KREUSLER and others (*Bied. Centr.*, 1880, 27—29).—Amongst the various methods employed for the cooking of fodder, none has hitherto been in use which does not diminish the quantity of nutritive matter and injure its digestibility; this frequently happens when it is sought to make the fodder more palatable and urge the animals to consume larger quantities. The usual methods are souring, fermenting, boiling, scalding,

and steaming. The first two occasion a loss of the raw material, the others diminish the digestibility and nutritive effect by the addition of large quantities of water. Steaming appears to be the least deleterious. Two oxen were chosen for purposes of experiment; the quantities given them were calculated from observation of their previous ordinary consumption. The experiments were divided into three periods, when the animals were fed first upon raw, secondly upon steamed, and thirdly on damped hay.

Their consumption of water does not seem to have been affected by the quantity taken up in the steamed or moistened fodder, the animals consuming their normal quantity.

From the calculated results of the droppings, it appears that the amount of protein substances digested in the raw and damped hay is about the same, and much greater than is found in steamed hay.

The authors summarise thus: the steaming of hay diminishes facility of digestion, is in fact injurious, and the desire of the animals for it, which has been asserted, is not found, but on the contrary, the animals liked the steamed hay less than either of the other kinds.

J. F.

**Permanent Pasture a Substitute for Clover.** By J. GODEFROY and others (*Bied. Centr.*, 1880, 50—53).—French agriculturists have for many years found the soil in some localities worn out, and, as it is called, "clover sick." On the other hand, foreign competition in cattle rearing forces them to raise large quantities of fodder materials. They have therefore turned their attention to laying down permanent pastures, or at least meadows for two to five years. The experiments of which this paper is the record, were carried out for this purpose, and were made at St. Ouen, near Pontoise, by two of the authors, and at Villeneuve le Roi by two others. The mixtures used were of English origin, consisting of leguminous and graminivorous plants, fescue rye-grass, &c. In one experiment the plot was divided into two portions, one of them being manured with stable manure, the other with artificial fertilizers; the latter gave far better results.

The observations are not complete, but so far they lead to the belief that it is quite possible to lay down meadows which will yield excellent crops the first year, with increasing produce the second and third years.

J. F.

**Composition of Red Clover and Maize.** By H. WATKIN and others (*Bied. Centr.*, 1880, 46—48).—The clover plants were 25 days old at the commencement of the observations, 24th May. Some of them bloomed on 21st June, and 5th July the flowering was general, and on 12th July it was nearly over. The nitrogen percentage declined until the time of bloom, remained tolerably constant for a short period, and then rapidly fell off; the behaviour of the cellulose was exactly the reverse. The sulphur and phosphorus compounds vary in much the same manner as the nitrogen, but not with such regularity.

The figures show a steady progression in productive power until the termination of the flowering period, when it ceases, except as regards the cellulose. Therefore, when the plants were in blossom,

about the 5th July would have been the most economical period to cut them.

The maize plants were observed from six days old, 24th May; the nitrogen diminished more quickly than in the case of the clover, and more rapidly in the first than in the second half of the period of observation. The diminution in the nitrogen was, however, not accompanied by so large a formation of cellulose as in the clover, a large proportion of the non-nitrogenous substances consisting of extractive matter: as the secretion of nitrogenous substances ceases at an early stage, the author thinks it economical to cut maize intended for green fodder not later than the end of August, as is actually the practice.

J. F.

**Nutritive Value of "*Elodea canadensis*."** By W. HOFFMEISTER (*Bied. Centr.*, 1879, 915—916).—This plant (the water pest) is greedily devoured by cattle; when fresh it contains 12, and when air-dried from 73—83 per cent. of solids. The composition of the solid constituents was found to be as follows:—

|        | Protein. | Fat. | Nitrogen<br>free extract. | Fibre. | Ash.  |
|--------|----------|------|---------------------------|--------|-------|
| 1 .... | 17.37    | 2.32 | 44.17                     | 16.98  | 19.22 |
| 2 .... | 19.56    | 2.26 | 41.48                     | 16.54  | 20.16 |

The percentages of cellulose and starch were found to be 16 and 19.4 respectively. In nitrogenous constituents, water pest compares favourably with clover.

J. K. C.

**Cotton-Seed Cake as Fodder.** By RITTER (*Bied. Centr.*, 1878, 902).—Ritter found that by using this cake, the cows yielded more milk and of a better quality.

J. K. C.

**Culture of the Lentil Vetch.** By E. v. RODICZKY (*Bied. Centr.*, 1880, 49—50).—This plant, known under various names, has always been considered in Germany a weed, *Vicia ervilia*. In sandy districts of Spain, parts of Switzerland, and in the south of France, it has sometimes been sparingly cultivated as a winter fodder. It appears to be less liable to injury from insects than peas and lentils, and can be cultivated without supports, a circumstance not without weight.

The author is not enabled from actual experiment to pronounce an opinion on the results of this crop under the climatic conditions of Germany, his analyses having been made on French, Spanish, and Grecian seeds.

Although the beans of this plant are a very valuable food, it is chiefly employed as a green fodder and as hay, the tender stems and numerous young fresh leaves rendering it peculiarly useful for the purpose. A partial experiment showed a result—2 hectoliters of seed per hectare after two months, when the plants were in bloom—13,700 kilos. green fodder, and 2,500 kilos. dry hay. Winter pease showed 4,500 and lentils 5,300 kilos. Considering the short time required to

bring this plant to maturity, and its suitability to light sandy soils, it is certainly worth some attention from practical farmers.

J. F.

**Seeds of the Corn Cockle as Fodder and Distillery Material.** By R. ULBRICHT (*Bied. Centr.*, 1880, 34—36).—The seeds of this plant, *Agrostemma Githago*, are largely bought by farmers on account of its low price as a fodder material, and is also offered to distillers, and sometimes purchased by them, notwithstanding it is known to have frequently had very injurious effects.

Analyses of two samples show the nutritive properties of the material to be very valuable, and in a chemical sense to stand about equally between grain and leguminous plants, a prominent feature being the large proportion of fat and the extraordinary quantity of mineral matter, particularly potash and phosphoric acid, which is higher than in any other grain yet analysed.

An old milch goat was fed with the grain of *A. Githago*, 300 to 500 grams given daily with clover hay. It was then fed for 12 days entirely on the seeds. During the whole of this period there was no disturbance of the animal's health, nor was the production of milk in any way lessened; but three weeks afterwards, when the animal had been put back to her normal food, she sickened and died; a post mortem showed severe inflammation of the large intestine and lesion of the spinal marrow.

A pig weighing 9·24 kilos., to whose food was added 20—100 grams of the seed daily, died in 14 days, and showed a strong inflammation of the coats of the stomach. Another and larger pig, weighing 12·32 kilos., was fed with gradually increased quantities of the material up to 350 grams per day, gained weight and continued in good health. Geese and ducks were also experimented on, but with negative results. The observations show that great caution is necessary in the use of this product for feeding purposes. The author believes that the poisonous principle may be extracted in a manner similar to that in which the bitterness is removed from lupins, but it is a thing of the future, and might at the same time diminish the value of the article as fodder.

The author made other experiments as to its value for distillery purposes, but they are incomplete.

J. F.

**Digestibility and Nutritive Value of the Soja Bean.** By H. WEISKE and others (*Bied. Centr.*, 1880, 30—31).—The experiments were made on two full grown Southdown wethers with the object of determining the food value of the article. Analysis shows the composition of the straw to resemble in valuable constituents that of good meadow hay, and analysis of the excrement of the animals shows that a large proportion was digested. The cultivation of this bean is very largely carried on in Germany; it yields a large produce, and these experiments prove it to be a valuable addition to the fodder materials at the farmers' command.

J. F.

**Flesh-meal as Fodder for Milch Cows.** By FEHLAU (*Bied. Centr.*, 1879, 599).—Flesh-meal added to other stall-fodder in the



daily proportion of 0·5 kilo. per cow, increased the yield of milk and the weight of the cow when compared with the results obtained from cows that received no flesh-meal, but its comparative action on the same cows was not ascertained.

A. J. C.

**Spent Hops as a Fodder for Cattle.** By M. MAERCKER and E. WEIN (*Bied. Centr.*, 1879, 601—602).—Spent hops are recommended as a valuable addition to rich nitrogenous cattle fodder, such as grains, &c., on account of the large amount of extractive matter they contain, viz., 45·06 per cent. soluble in water, which contained 14·71 per cent. sugar from the wort; 3·30 per cent. protein, and 2·05 ash. Wein's analysis further showed water 11·6 per cent., fat 4·52 per cent., ash 3·39 per cent., protein 14·06 per cent., fibre 16·39 per cent., non-nitrogenous matter 50·08 per cent. (see also this Journal, *Abst.*, 1879, 1050).

A. J. C.

**Spent Hops as Fodder.** By H. WEISKE and others (*Bied. Centr.*, 1879, 906—908).—Further researches confirm the results already published that spent hops do not make good fodder, although in unfavourable seasons they may be useful.

J. K. C.

**Cacao Rind as Fodder for Calves.** By SAMEK (*Bied. Centr.*, 1879, 946).—The milk was gradually replaced by extract of cacao rind in the fodder of calves. The animals appeared to thrive on the change of diet, although they showed considerable distaste for it. An analysis of the pulverised rind gave the following results. In 100 parts substance:—

| Water. | Ash. | Protein. | Fat. | Fibre. | Nitrogen<br>free extract. |
|--------|------|----------|------|--------|---------------------------|
| 11·13  | 7·28 | 25·87    | 8·22 | 13·35  | 34·15                     |

J. K. C.

**Influence of the Potato Blossom on the Amount of Produce.** (*Bied. Centr.*, 1879, 634).—208 centrs. 19 lbs. of tubers were obtained from potato plants from which the blossom had been removed and only 181 centrs. 49 lbs. of tubers from plants not so treated.

A. J. C.

**Growth of Beets.** By P. BEHBEND and A. MORGEN (*Bied. Centr.*, 1879, 612—613).—The results of the analyses show that a better produce was obtained from a sandy soil than from a beet soil. The amount of sugar in the two cases from two varieties of beets was from a sandy soil 10·46 and 13·90 per cent., from a beet soil 8·35 and 8·39 per cent.

A. J. C.

**Planting of Sugar Beets.** By J. HANAMANN (*Bied. Centr.*, 1879, 614—617).—The experiments were made on seven different kinds of soil and with seed under various conditions of sowing, and the results confirm what has been stated previously by other observers that in thick sowing—in the author's experiments the minimum area to each plant was 555 square cms. and the maximum 1,000 square cms.—the produce

of the beet crop is smaller in quantity, but of higher value in the amount of sugar and in the density and purity of the juice than in thin sowing. According to the space allotted to each plant it was found that on one and the same soil the sugar quotient varied from 86—91 per cent. and in another case from 88—93 per cent., and this important sugar factor is said to be more affected thereby than by the manuring or even by the kind of beet grown. The distance between the plants should be small on a humid and matured land, but great on a dry, high ground and poor soils.

A. J. C.

**Results with Stall-feeding of Sheep.** By F. SCHNORRENPFEL (*Bied. Centr.*, 1880, 33—34).—The feeding of 10 sheep for purposes of exhibition allowed the following comparison between the results of their luxurious feeding and that of other members of the same flock ordinarily foddered. The flock consisted of 247 Southdown Merinos, which were well fed and cared; five of the best formed wethers and five two-year old ewes were carefully selected for stall-feeding. Up to 13th of January they received the same food as the remainder of the flock, and on that day were shorn and yielded 3·875 kilos. of wool in the grease; from this day they had unlimited supplies of peas, linseed cake, and rye bread, out of constantly replenished mangers. Each day they were littered and fed four times, and each morning the litter removed. From the beginning of May, in order to increase their appetite, the turnips and acorns were sliced and pared and the crust removed from the bread; about the 20th of May the animals took an instinctive dislike to over-feeding, but it was continued, and on the 11th of November the 10 sheep were valued; the result was, all costs of feeding calculated, a surplus of the stall-fed over the ordinary sheep of 15·14 marks each.

The author thinks that it would pay the farmer to liberally nourish sheep of good breeds with food similar to human food and in large quantities, even so far as to supply it *ad libitum*, if the farmer could find a ready outlet for the unconsumed fodder.

J. F.

**Decomposition of Silicates.** By J. LEMBERG (*Bied. Centr.*, 1879, 567—577).—In the first part of the original paper, of which this is an abstract, the author gives a series of analyses of minerals in various conditions of decomposition. His experiments on the absorptive power of soils lead him to the conclusion that it is a purely chemical action, in which the influence of mass is to be regarded according to Berthelot's views. On account of the complex character of soils and the different behaviour of one and the same silicate towards different solutions of salts, it is impossible to express the absorptive action by an empirical rule. The decreased absorptive power which a calcined soil has, cannot be due to the decomposition of humus substances or to an alteration in the capillarity of the soil. It is even possible that many kinds of soils have their absorptive power for some substances increased after calcination.

By treating a potassium silicate with an aqueous solution of carbonic acid, the greater part of the potash is abstracted, hence it is

assumed that basic water has been substituted for the potash, and as a silicate so treated can re-absorb the base, the author concludes that the strong absorptive power of such soils for free potash is partly due to the re-formation of the decomposed silicate by the substitution of basic water by the fixed base. This action is more complicated in the soil, as a part of the potash combines with free silicic acid to form a soluble silicate, which again combines with hydrated alumina and kaolin compounds; therefore it would be expected that a calcined soil having lost its basic water has undergone a great decrease in its power to absorb free potash.

The supposition that potassium carbonate, when brought into contact with a silicate which has been deprived of the greater part of its potash by the action of carbonic acid water is partly decomposed into free carbonic acid and potash, which latter is taken up by the silicate, was confirmed by a series of experiments which showed that the silicate behaved in fact as an acid salt, the carbonic anhydride and the silicate being apportioned to the potash according to their mass and affinity. The substitution of basic water by a fixed base, and moreover the possibility of the direct addition of alkaline carbonates to silicates without substitution, explain the fact that in many cases more substances are absorbed by a soil than correspond with the substances eliminated. As ammonia behaves similarly to potash in the replacement of basic water in silicates, the absorption by a soil of free ammonia cannot be regarded as favouring the theory of mechanical absorption, nor can the retention by a soil of easily soluble salts. W. Knop's method for estimating humus substances in soils (*Landw. Versuchs.-Stat.*, 8, 40), which consists in treating the soil with an ammoniacal solution of calcium nitrate and calculating the amount absorbed as calcium humate, would, according to the author's statement, give incorrect results, as silicates containing basic water behave like weak acids, and in this case would retain the lime which would be incorrectly calculated as humate.

The author controverts at some length the various points which are alleged by some observers to be evidence in favour of the theory of mechanical absorption. It is evident that silicates in soils undergo the same metamorphosis as all other minerals without exception, but a part of the silicate is specially prone to enter into chemical exchange with dissolved substances. Silicates of the zeolite class are among the most rapid absorbents, and on this account Mulder has placed the absorbing silicates in this category; but this property is not confined to zeolites, being possessed by several feldspatic silicates.

The author disagrees with the statement of A. Knop that micaceous silicates are produced in a soil by the absorption of potash, also with the supposition that the degree of absorption is in concordance with the amount of bases dissolvable by dilute acids, showing that although silicates, which quickly undergo change with solutions of salts, are easily decomposed by weak acids, yet the contrary fact does not necessarily follow. The degree of absorption is quite arbitrary, and depends rather on the substance employed; some constituents of soils can quickly absorb potash, others again behave altogether differently. It is rather the rule that minerals which are decomposed with difficulty

by acids very slowly undergo chemical change, but this only occurs so long as the period of action is proportionally short.

Potash is more readily absorbed by soils and silicates than lime, magnesia, or soda. If a silicate which contains potash and soda be decomposed by carbonic acid water, the soda is always the first base abstracted; again, the latter is frequently replaced in a soil by potash, but potash is seldom replaced by soda.

The fusion of silicates with fusible salts of the alkalis, alkaline earths, and of iron, is analogous in its chemical action to that of an aqueous solution of the salt at the ordinary temperature.

A. J. C.

**Free Carbonic Anhydride in Soils.** By J. MÖLLER (*Bied. Centr.*, 1879, 631).—The amount of carbonic anhydride in the air in soils is not much above that contained in the atmosphere. Organic soils contain in themselves a constant source of carbonic anhydride, and the external conditions remaining the same its formation there proceeds without much variation. Dry quartz sand has not the property like other kinds of soils of condensing carbonic anhydride, the amount of which in soils is dependent to a great extent on the porosity of the soil and the nature of its stratification. It decreases in amount as the soil dries up, but a damp soil produces as much as a soil saturated with water; rainfall causes an increase at first, but it quickly declines in proportion to the rate of surface-evaporation; the carbonic anhydride absorbed by the rain is set free and enriches the atmosphere of the soil. The amount of carbonic anhydride does not perceptibly increase with the depth of the soil; it is higher in unmanured than in manured soils.

A. J. C.

**Clover Sickness.** By A. EMMERLING and R. WAGNER (*Bied. Centr.*, 1879, 578—582).—The results of the analyses of the soil and of the ash of the affected red clover at first seemed to indicate that the cause of the disease was due to the pooriness of the soil in potash, but further investigation, more especially the results obtained with white clover growing in the same soil, showed that no direct conclusions could be drawn from the chemical examination. In this particular instance the clover sickness is ascribed to a want of proper culture of the plant. Red clover requires a matured soil, deeply tilled, damp, and in good culture; it seldom repays direct dunging. The land had only been for a short time in cultivation, and having regard to its stony nature had not been tilled sufficiently deep; whilst in many parts the soil was poor in humus, and contained an abundance of lime, a state conducive to sterility. The general conditions of the soil being unfavourable to the growth of red clover, the plant was less able to endure the poverty of the soil in potash.

White clover requires very different conditions; it thrives in soils not so deep and less cultivated, and once planted, it withstands the summer droughts.

The remedy to be generally applied is to increase the amount of humus and nitrogenous matter, to give a supply of phosphoric acid and potash with greater depth of soil.

The poorness of the soil had exercised no perceptible influence on the composition of the organic constituents of the clover.

A. J. C.

**Manures for Cabbages and Fruit Trees.** By LAUCHE (*Biedl. Centr.*, 1879, 591—593).

**Amount of Nitrogen in Forest Trees, and in the Under Litter of Leaves.** By J. SCHRODER (*Biedl. Centr.*, 1879, 634—635).—The average amount of nitrogen required to be supplied to forest trees is about equal to that given to stalk crops in the form of manure. This is supplied to the former in the under litter of leaves, which serves the same purpose to the trees as artificial manures to field crops, both in its supply of nitrogen and ash constituents. Hence the importance of not removing the under litter.

A. J. C.

**Employment of Peat as Manure.** By T. NERLINGER (*Biedl. Centr.*, 1879, 883—885).—Direct application of peat alone to sandy soils does not give such good results as to allow of dispensing with other kinds of manure, although the yield obtained is greater than if the soil had not been manured at all. The author recommends that before use the peat should be first mixed with lime and stable drainings.

J. K. C.

**Guano from the Island of Ichaboe.** By B. C. NIEDERSTADT (*Landw. Versuchs.-Stat.*, 24, 269—270).—The guano is quite recent as a rule; the nitrogen is mainly in organic combination. An original sample, known in commerce as "ammonia-fixed Ichaboe guano," No. 2, was analysed with the following result:—

| CaO.  | Fe <sub>2</sub> O <sub>3</sub> . | MgO. | Sand. | KCl. | NaCl. | P <sub>2</sub> O <sub>5</sub> . |
|-------|----------------------------------|------|-------|------|-------|---------------------------------|
| 21.04 | 1.52                             | 0.65 | 3.35  | 1.40 | 3.25  | —                               |

Total, 11.25 (8.13 soluble, 3.12 insoluble); organic compounds, 21.46 (with 7.99 of N, of which 2.89 was present as ammonia); SO<sub>3</sub>, 20.33, moisture at 105°, 15.75 per cent. = 100.00.

J. T.

**Natural Phosphates and their Value in Agriculture.** By J. HANAMANN (*Biedl. Centr.*, 1879, 631—632).

**Experiments with Artificial Manures.** By v. BULOW (*Biedl. Centr.*, 1880, 18—21).—This paper gives the results of certain experiments on manuring potatoes and beetroots, carried out at the instance of an agricultural society in Posen.

For the potatoes, the soil was well dug in with strong stable manure in the autumn, left fallow until the following May, and then divided into three portions, the first of which received no artificial manure, the second was treated with nitrate of soda only, the third received equal parts of 20 per cent. superphosphate and nitrate of soda. The several quantities dug were:—Unmanured plot, 89, Schifflast; nitrate, 102; nitrate and superphosphate, 107. It follows that the employment of nitrate of soda with potatoes pays, the addition of superphosphate increases the yield, but at a greatly augmented cost, and could only be

recommended on large distillery farms, where the freight of a quantity would be an appreciable consideration.

In the experiments with beetroots, a very similar course was pursued. In the autumn, the plot which contained some unfavourable soil, was well tilled with plenty of cowdung. In the spring of the following year, three plots were measured off, and all treated with artificial manures. No. 1 with 100 lbs. superphosphate; No. 2, 100 lbs. superphosphate, and 400 lbs. kainit; No. 3, 100 lbs. superphosphate, and 150 lbs. nitrate soda; another plot received no artificial manure; the seeds were carefully sown and tended, hoed, and cultivated. The results were: without artificials, 200 50 centner; with superphosphate, 226 92; superphosphate and potash, 243; superphosphate and nitrate soda, 259·70.

Everything calculated and allowed for, the additional cost of the artificial manures was fully paid, and the three plots left a surplus; the superphosphate paid the best, and in localities where beets are largely raised, and the value of them at least 1 mark per centner, superphosphate would amply repay liberal use. J. F.

**Chili Potash Saltpetre.** By G. DRECHSLER (*Bied. Centr.*, 1879, 582—584).—The application of this manure, which contained 34·26 p.c. potassium nitrate, and 56·18 p.c. sodium nitrate, to sugar beets, increased the amount of sugar in the beet by 2·11 and 1·47 p.c. above that yielded by beets that were unmanured and manured with Chili saltpetre respectively. A. J. C.

**Manure Experiments with Superphosphate and Chili Saltpetre.** By COUNT SCHWERIN-PUTZAR (*Bied. Centr.*, 1879, 584—585).—Chili saltpetre as a manure for rye, especially on ill-conditioned land, gives a greater produce than superphosphate. A. J. C.

**Lupine Seeds as a Manure.** By A. SELMI, C. COSTA-REGHINI and F. OPPENAU (*Bied. Centr.*, 1879, 585—587).—An experimental inquiry as to the relative value of lupine seeds in comparison with bone meal and linseed cake meal mixed with sewage, in which the results are in favour of the first named. Details are given, showing the pecuniary profit accruing from the produce (beans and maize) by the use of each kind of manure. A. J. C.

**Action of Various Manures on the Composition of Must.** By E. ROTONDI and A. GALIMBERTI (*Bied. Centr.*, 1879, 590—591).—The manures employed were respectively lime phosphate, a mixture of equal parts of lime phosphate, potassium nitrate, and gypsum; potassium nitrate, potassium chloride, sodium nitrate, and ammonium sulphate. The conclusions are (a) that the must of the manured vines is slightly richer in sugar than that of the unmanured; (b) potash in combination with chlorine appears the most materially to increase the amount of sugar in the must; (c) lime phosphate apparently increases the tartar, and lessens the amount of free tartaric acid. There is no relation between the total acidity of the must and the manure employed.

The ash of the must was increased by all the manures, more especially by potassium chloride, and less so by sodium nitrate.

A. J. C.

**Manuring Experiments on Wheat and Rye.** By A. THAER (*Bied. Centr.*, 1879, 945).—The manures used were as follows:—Decomposed guano, with 10 p. c. of soluble phosphoric acid, and the same quantity of nitrogen; dried bone-meal, with 20 p. c. of phosphoric acid. From each half acre were obtained—

*Wheat.\**

|                 | Grains.<br>Kilos. | Straw.<br>Kilos. | Chaff.<br>Kilos. | Total.<br>Kilos. |
|-----------------|-------------------|------------------|------------------|------------------|
| Unmanured.....  | 161.0             | 340              | 43.0             | 549              |
| With guano..... | 232.5             | 480              | 60.5             | 773              |

*Rye.*

|                   |       |     |    |        |
|-------------------|-------|-----|----|--------|
| With guano.....   | 251.0 | 720 | 45 | 1016.0 |
| With bone-meal .. | 222.5 | 714 | 42 | 983.5  |

J. K. C.

**Manuring of Oats.** By BRENNING (*Bied. Centr.*, 1879, 881—882).—The soil on which the experiments were conducted had been sown in 1877 with potatoes, and in 1878 with rye. In the spring of 1879 it was divided into eight plots, of 518 square meters each, and treated in the following way:—No. 1 was unmanured; No. 2 received 3.75 kilos. soluble phosphoric acid; No. 3 was manured with 2.25 kilos. nitrogen as ammonia, and 2.25 kilos. soluble phosphoric acid; No. 4, with 5 kilos. soluble phosphoric acid (as guano-superphosphate); No. 5, 2 kilos. nitrogen, as nitrate of soda; No. 6, 1.95 kilo. nitrogen (in the form of decomposed guano), and 7.38 kilos. soluble phosphoric acid; No. 7, 1.75 kilo. nitrogen, and 2.38 kilos. soluble phosphoric acid, both in the form of decomposed guano; No. 8, 1.95 kilo. soluble phosphoric acid, and 1.60 kilo. nitrogen as nitrate of soda.

The oats on plots 3, 5, 6, 7, and 8 thrived the best, having a darker colour and better growth than the plants on the other plots. On plot 4, the plants had during the whole time of growth a very poor appearance, and were more backward than those on the unmanured plot. The following yields were obtained:—

| Plot.   | Good oats.<br>Kilos. | Poor oats.<br>Kilos. | Total<br>weight of<br>corn.<br>Kilos. | Straw.<br>Kilos. | Chaff.<br>Kilos. |
|---------|----------------------|----------------------|---------------------------------------|------------------|------------------|
| 1 ..... | 147.0                | 15.5                 | 162.5                                 | 312.5            | 11.5             |
| 2 ..... | 145.5                | 6.0                  | 151.5                                 | 283.0            | 10.0             |
| 3 ..... | 166.5                | 17.5                 | 184.0                                 | 346.0            | 12.5             |
| 4 ..... | 110.0                | 8.0                  | 118.0                                 | 205.75           | 11.25            |
| 5 ..... | 170.0                | 12.5                 | 182.5                                 | 325.0            | 10.0             |
| 6 ..... | 149.5                | 12.0                 | 161.5                                 | 309.0            | 10.0             |
| 7 ..... | 159.5                | 8.0                  | 167.5                                 | 320.0            | 15.0             |
| 8 ..... | 156.0                | 11.0                 | 167.0                                 | 250.0            | 13.0             |

J. K. C.

**Manuring of Beetroots.** By J. HANAMANN (*Bied. Centr.*, 1879, 917—919).—As the results of three years' experiments on the manuring of beet, the author finds that in the ripe plant there is a constant relation between the sugar produced and the potash absorbed by the root of about 100 to 2; and that a strong nitrogenous manure in a calcareous soil produces the same effect as potash. No constant relation between the phosphoric acid and sugar was observed. J. K. C.

**Effect of Manures on Growth of Larches and Pines.** By HESS and L. HAMPEL (*Bied. Centr.*, 1880, 21—23).—This paper gives the results of two sets of experiments; one by Hess, on the effect of manures on the growth of larch seedlings, carried out in the Collegiate Gardens at Giessen; and the other by L. Hampel on pine seedlings, at Gusswerk, in Austria.

In both cases, three garden beds were prepared, one left unmanured and the other two manured. The results show a balance in favour of the latter, but the differences are not very striking and the experiments not sufficiently extensive to base any broad conclusions on.

J. F.

## Analytical Chemistry.

**Method of Measuring High Temperatures.** By J. M. CRAFTS and F. MEIER (*Compt. rend.*, 90, 606—608).—This method is designed specially to determine the temperature employed when using V. Meyer's method of determining vapour-densities, but is generally applicable to other cases. A tube of glass or platinum is passed down to the bottom of the apparatus, and the air is driven out by a current of some easily absorbable gas, collected in a eudiometer, and measured at the ordinary temperature. The vapour-density determination is made immediately afterwards in the same apparatus, as soon as the gas has been displaced by dry air or nitrogen. Hydrochloric acid gas is preferable, since its complete absorption by water serves as an indication of the total expulsion of the air. This gas does not attack glass or porcelain vessels, and is not dissociated at 1300°. In calculating the temperature, the apparatus must be regarded as consisting of two parts, one of which is at the temperature to be measured, whilst the other is at some lower temperature. The method gives satisfactory results. C. H. B.

**Detection and Estimation of Chlorine in presence of Iodine and Bromine.** By G. VORTMANN (*Ber.*, 13, 325—326).—The method proposed is based on the different behaviour of the halogen elements towards the peroxides of lead and manganese in the presence of acetic acid. Iodides are decomposed by the oxides even in a neutral solution, and the separation of the iodine is complete if the liquid be boiled with acetic acid. When peroxide of lead is employed, a portion of the



iodine is converted into iodic acid, whereas this is not the case with peroxide of manganese. Bromides are not decomposed by either oxide in a neutral solution. In acetic acid solution only the lead peroxide causes the separation of the bromine, the other oxide having no action, and only in the presence of large quantities of bromine is any bromic acid formed. Chlorides, on the other hand, are affected by neither oxide either in neutral or acetic acid solution.

In order to detect chlorine then in the presence of the other halogens, the substance is boiled with lead peroxide and acetic acid until the liquid becomes colourless, and smells no longer of bromine or iodine, any iodic acid which may have been formed is got rid of by filtering the mixture from the lead iodate and the excess of oxide used. The filtrate now contains all the chlorine free from both bromine and iodine. The method also serves for the quantitative determination of chlorine in presence of the other two halogens.

When the chlorine is present in large quantity together with iodine, it is better to use manganese peroxide so as to avoid the formation of the difficultly soluble lead chloride; and when there is a large quantity of chlorine together with bromine, a little potassium sulphate should be used along with the lead peroxide, so that all the chloride may be present as potassium salt.

T. C.

**Parkes's Method of Estimating Copper.** By R. ULBRICHT (*Landw. Versuchs.-Stat.*, 24, 253—267).—The first and only part here given of an article on *must and wine analyses* is taken up with detailed results of an examination of Parkes's method. Very good results are obtained when the standardising of the cyanide solution and titration of the copper solution are made under the same conditions, that is, when in both cases the same quantity of nitric acid, the same quantity of free ammonia, and the same quantity of ammonium salts are present; also when the resulting solutions have the same volume, the cyanide solution is added in the same time and in the same manner, and the amount of copper is about the same in both. The cyanide solution is standardised daily. Under these conditions the method serves very well for the determination of the copper precipitated by Fehling's sugar determination process.

J. T.

**Use of Smithson's File for the Detection of Mercury in Mineral Waters.** By J. LEFORT (*Compt. rend.*, 90, 141—143).—Orfila objected to the voltaic couple of tin and gold, devised by Dr. Smithson for the detection of small quantities of mercury, alleging that when it was allowed to remain for some time in the suspected solution, traces of tin were dissolved, which, re-depositing upon the gold plate, caused the latter to become whitened even in absence of mercury.

The author shows that this deposition of the tin is liable to take place, but that no real error can result, since the metal not being volatile cannot be sublimed, there is therefore no sublimate to be submitted to the vapour of iodine, whereby an essential part of the operation as conducted by Smithson is omitted. Such, however, is not the case with arsenical solutions; the arsenic deposits upon

the gold with great readiness, and the coated foil when heated in a closed tube, yields a sublimate, which, although not exactly resembling the mercurial sublimate, becomes red from formation of arsenic iodide, when acted on by iodine vapour. The colour of the arsenic iodide under these conditions is very similar to that of mercuric iodide, and it becomes necessary to use the microscope in order to distinguish them.

The water from the Rocher spring at St. Nectaire (Puy-de-Dôme) was examined by this process some time ago, and was stated to contain mercury; this statement is now contradicted, it being shown to contain arsenic and not mercury.

In a similar manner, the presence of arsenic has been detected in the mineral water of Bourboule; and doubtless this element might be shown to be present in many other waters if they were carefully examined by this process, or by some other method of equal delicacy.

J. W.

**Separation of Minerals of Greater Density than Quartz, by means of Fused Mixtures of Lead and Zinc Chlorides.** By R. BRÉON (*Compt. rend.*, 90, 626—627).—The density of lead chloride in a state of fusion is 5, of zinc chloride 2·4; by mixing these two substances, a liquid of any required density between the two extremes is easily obtained and may be employed to separate minerals of different densities. The mixture of salts is fused in a test-tube, and the powdered mineral is thrown in little by little: after some time the tube is allowed to cool, and is then broken. In this way, a solid cylinder is obtained in which the various minerals are arranged in the order of their densities. The lead and zinc salts may be easily removed by boiling with pure water or with dilute acetic acid.

C. H. B.

**Physico-chemical Analysis of Clay-soils.** By F. SESTINI (*Gazzetta*, 10, 57).—The author regards Schloesing's method (*Compt. rend.*, 78, 1276), although tedious and troublesome, as the only one which permits of a satisfactory determination of the amount of clay in a soil. He finds, however, that it is better to give twelve washings instead of six, and to diminish the time of settling from 24 to 12 hours. He also recommends that a camel's hair pencil should be used when rubbing up the soil with the water. In this way very satisfactory results are obtained.

C. E. G.

**Physico-chemical Analysis of Clay-soils.** By N. PELLEGRINI (*Landw. Versuchs.-Stat.*, 25, 48—52).—The author compares the methods of Noebel and Schloesing. With a clay-soil from Orciano, near Pisa, Noebel's method gave sand 1·471 per cent., clayey constituents 87·315, soluble and loss 1·560, organic and volatile 9·654. Schloesing's for the same clay gave sandy constituents 32·075 per cent., clayey 37·670, earthy carbonates 20·200, organic and volatile 10·255. With the same soil, Masure's method gave sandy constituents 13·358, clayey constituents 71·899. Knop's method, sandy constituents 21·208, clayey constituents 64·432; the differences are enormous. Schloesing's method is the best.

J. T.

**Estimation of Glycerol in Wine.** By H. RAYNAUD (*Bull. Soc. Chim.* [2], 33, 259—262).—The wine is evaporated to one-fifth of its original volume, and the alkalis precipitated with hydrofluosilicic acid and alcohol. The filtered solution is treated with a slight excess of baryta, mixed with sand and evaporated in a vacuum. The residue is extracted with a mixture of equal volumes of alcohol and ether; the extract is evaporated, and the residue kept in a vacuum over phosphoric anhydride for 24 hours to eliminate the last traces of moisture and then weighed. The glycerol obtained sometimes leaves an ash on evaporation. The impure glycerol, after extracting the alkalis, does not contain one-tenth of its weight of non-volatile substances.

L. T. O'S.

**Estimation of Glucose.** By BATTANDIER (*J. Pharm. Chim.* [5], 1, 221—222).—Glucose in urine may be estimated with greater certainty by using ammoniacal Fehling's solution than with the ordinary solution. 100 c.c. of Fehling's solution are treated with 250 c.c. ammonia, and the mixture made up to 1 liter. 200 c.c. of this solution (= 0.10 grain glucose) are put in a flask, provided with a cork in which two tubes are inserted, one is connected with a Mohr's burette containing the urine, the other allows access to the air. The contents of the flask are brought to boiling, and the urine added drop by drop from the burette until the colour of the solution disappears.

L. T. O'S.

**Volumetric Estimation of Sugar by an Ammoniacal Copper Test, giving Reduction without Precipitation.** By F. W. PAVY (*Proc. Roy. Soc.*, 28, 260).—By adding ammonia to Fehling's solution, a clear blue solution is obtained which is reduced by sugar to a perfectly colourless solution without any precipitation of cuprous oxide. With the solution prepared in this way, it is found that 1 atom of sugar reduces 6 atoms of cupric oxide instead of 5. When, however, caustic potash, in the proportion of 5 grams to 20 c.c. of the ammoniated test (one-tenth of Fehling's solution), was added, the amount of copper reduced was brought back to the normal 5 atoms.

C. W. W.

**Estimation of Starch in Potatoes.** By SIEWERT (*Landw. Versuchs.-Stat.*, 24, 427—434).—The author criticises methods given by Heidepriem and Holdeffleiss, and remarks that his results differ from those of Maercker. He treats the potato cut up into small pieces with  $1\frac{1}{2}$  per cent. solution of tartaric acid for four hours on a paraffin-bath at  $112-115^{\circ}\text{C}$ ., shaking it frequently. After cooling, it is made up to a fixed volume, filtered, and a measured volume again heated gradually with 30 drops of concentrated sulphuric acid up to a temperature of  $112-115^{\circ}\text{C}$ ., by which the sugar becomes inverted. A slight excess of Fehling's solution is used, and the cuprous oxide filtered off, roasted for  $1-1\frac{1}{2}$  hours, and weighed until constant.

By this process, the use of diastase and two sugar determinations is avoided. At a lower temperature than  $110^{\circ}\text{C}$ ., and in less than four hours, all the starch is not converted into sugar; whilst at a temperature above  $115^{\circ}\text{C}$ ., the liquid begins to be discoloured: on heating for six hours, most of the sugar is inverted.

J. T.

**Estimation of Starch in Potatoes.** By P. BEHREND, M. MAERCKER, and A. MORGEN (*Landw. Versuchs.-Stat.*, 25, 107—165).—The authors find that all the starch can be extracted by water alone by heating at 135—140° C. for four hours, and after cooling to 90°, filtering it quickly through an asbestos plug by the aid of a Bunsen pump. To convert into sugar, the filtrate is heated with hydrochloric acid on the water-bath for three hours. After nearly neutralising with potash solution, lead acetate is added, the precipitate separated by filtration, and the excess of lead removed by sulphuric acid. The sugar is determined by Fehling's solution, which only gives good results when used under constant conditions. The precipitated copper oxide is reduced in hydrogen and weighed as metal. Working always with the same volume of Fehling's solution and sugar solution, the amount of sugar is obtained from the weight of copper by reference to a curve previously prepared.

The amount of starch averages about 5.75 per cent. less than the dry substances in the potato, but the amount can only be very roughly estimated from the specific gravity. J. T.

**Estimation of Urea.** By A. FAUCONNIER (*Bull. Soc. Chim.* [2], 33, 103—105).—On repeating the experiments of Mehu on the action of alkaline hypochlorites and hypobromites on urea in presence of saccharose and glucose, the author confirms the results of Esbach, that the theoretical quantity of nitrogen is not evolved when saccharose is present; but in presence of glucose, results corresponding with theory were obtained. This is due to the formation of a small quantity of nitric acid which is reduced by glucose, but not attacked by saccharose. L. T. O'S.

**Estimation of Urea in Urine.** By JAY (*Bull. Soc. Chim.* [2], 33, 105—106).—The quantity of gas evolved by urea when treated with sodium hypobromite, is influenced by the quantity of cane-sugar present, notwithstanding that cane-sugar alone when treated with sodium hypobromite yields no gas. When grape-sugar is treated with sodium hypobromite, appreciable quantities of gas are evolved; consequently, neither cane-sugar nor glucose can be employed in the determination of urea. L. T. O'S.

**Lactic Fermentation.** By P. CAZENEUVE (*J. Pharm. Chim.* [5], 1, 212—215).—Saccharose, glucose, and lactose, in presence of urine in which the urea is converted into ammonium carbonate, undergo lactic fermentation, which, if sufficient sugar is present, continues until all the ammonia is converted into ammonium lactate. The microscopic examination has shown that besides bacteria, the lactic ferment discovered by Pasteur is present; and experiment proves that dilute urine is best suited for its development. In estimating glucose in diabetic urine, errors are likely to occur from this source.

L. T. O'S.

**Estimation of Non-albuminous Nitrogen-compounds in Plants.** By O. KELLNER (*Landw. Versuchs.-Stat.*, 24, 439—453).—The author discusses various methods, but gets the best results with

the following :—Ten grams of the finely pulverised substance is heated for  $1\frac{1}{4}$ — $1\frac{1}{2}$  hours with 300 c.c. of a 30—40 per cent. solution of alcohol containing a few drops of acetic acid; after cooling, an aliquot part is taken, filtered, evaporated, taken up with water, and treated with lead acetate to precipitate albuminous compounds. Kern proposed phosphotungstic acid, instead of lead acetate, but the author found that they gave almost identical results, except in the case of plants containing alkaloids, as peptones were found to be absent from the extracts, or present in traces only. The different results given by the two methods will serve as a direct measure of the amount of alkaloid nitrogen present in the plant during the period of flowering and afterwards; but during earlier plant-life, the presence of peptone, not precipitated by lead acetate, gives a difference in the results. To the alkaloids and peptones, a third nitrogen-compound must be added, whose presence has frequently been observed, namely, nitric acid; in cases where it occurs, a slight loss in nitrogen may result on evaporating the acid plant extract, due to the reaction of nitric acid on amides. The nitrates should be decomposed before evaporating by dropping the extract into a solution of ferrous chloride, mixed with hydrochloric acid, and heated on the water-bath; the residue is heated for ten minutes at a temperature of  $100^{\circ}$ . The nitrogen is then determined in the residue.

J. T.

**Analysis of Milk.** By L. JANKE (*Bied. Centr.*, 1879, 927).—The author remarks that a very large number of analyses at various times should be made for each locality, in order to fix a minimum in the quality of the milk. Out of 103 samples, the poorest milk had a sp. gr. of 1.0275, 9.04 per cent. of solids and 1.60 per cent. of fat.

J. K. C.

**Adulteration of Coffee with Chicory.** By PRUNIER (*J. Pharm. Chim.* [5], 1, 222—224).—To detect the presence of chicory in coffee, the microscopic examination is the best method, but as this is not always possible, the following method may be employed. The ground coffee is spread on a sheet of white paper. The grains of coffee present an angular fracture, whilst chicory has an amorphous appearance, and is of a darker colour; the suspected grains are picked out with a needle; the coffee grains jump away from, or are split by it, whereas the chicory grains, being softer, are easily penetrated. The softer grains when crushed carefully between the teeth produce a gritty sensation like fine sand. If chicory is present, its flavour also is more of an acid bitter, than the aromatic bitter taste of coffee.

Chicory may be estimated in coffee as follows:—About 2 grams of dried ground coffee are sifted in a hair sieve from the fine dust, which consists of pure coffee; the larger grains are macerated with cold water for some hours, and then thrown on a piece of stretched cloth and rubbed with the fingers, when the chicory is forced through, whilst the coffee grains remain on the cloth. The coffee is then collected, dried, mixed with the dust, and weighed; the loss in weight gives the weight of chicory.

L. T. O'S.

**Determination of Wine-extract.** By NESSELER (*Landw. Versuchs.-Stat.*, 24, 284—289).—The amount of extract may vary from 1·2 per cent. to 3 per cent. or more; 1·7 per cent. may be taken as a normal amount, and it may be made up as follows:—Non-volatile acids, 0·5; salts, albuminoids, and other constituents, 0·5; glycerol, 0·7; acetic acid, which boils at 120°, is often present in wine, a considerable amount of it goes off during the evaporation, but the last portions are not expelled by several hours' drying. The presence of glycerol causes a loss of weight during the drying at 100°; 1 gram of glycerol lost on an average 0·43 gram per hour for 18 hours. It is not advisable to heat until all the glycerol is expelled, and so to exclude it from the extract. The author proposes evaporating to a syrup, and then heating at 100° for four hours.

The following process is employed at the Versuch-Station, Weisbaden:—A weighed porcelain-boat, charged with dry quartz-sand, is heated in the water-bath, and 5 c.c. of wine are slowly dropped into it. The boat is then placed in a stream of coal-gas previously passed over calcium chloride. The boat is then cooled and weighed.

Halenke evaporates for six hours on the water-bath, and then stands in a vacuum over sulphuric acid for twelve hours. J. T.

## Technical Chemistry.

**Rapidity of Germ-diffusion in the Air.** By I. SOYKA (*Biel. Centr.*, 1880, 71—72).—The close connection between putrefactive and disease germs led the author to make some experiments intended to test the rapidity of dissemination of the former. The apparatus employed was of extreme simplicity, consisting of a pear-shaped flask partly filled with a solution of meat extract. Into this flask was led a tube which communicated with the outer air, first passing over a quantity of dried and powdered putrid blood. The air did not pass *through* the solution which was being experimented on.

The experiments were made with air currents of different velocities, and the author found it impossible to determine minimum rate of speed which would not convey the germs. He concludes that a very slight motion of the air almost, if not altogether imperceptible, is sufficient to convey them; much, however, depends on the lightness of the putrefactive matter, and the liability of the receptive substance to infection. He asserts also, and this appears worthy of further investigation, that when the air is thoroughly saturated with aqueous vapour, the putrefactive effects were not visible. J. F.

**Antiseptic Action of Salicylic Acid.** By A. SCHULTZ (*J. pr. Chem.* [2], 21, 380—382).—In order to ascertain what substances combine with salicylic acid, the author has treated solutions of bodies tabulated below, with given weights of salicylic acid. The amount of unaltered acid was determined by extracting the solutions with a given

volume of ether, and that of the combined acid by extraction with ether after acidifying with hydrochloric acid.

I. *Nitrogenous Substances*.—Asparagine, amygdaline, allantoin, urea, albumin, and gelatin.

II. *Organic Salts*.—Ammonium tartrate, sodium tartrate, Rochelle salt, dipotassium tartrate, potassium hydrogen tartrate, calcium tartrate, ammonium, sodium, and potassium malates.

III. *Inorganic Salts*.—Ammonium, sodium, and potassium phosphates, calcium pyrophosphate, ammonium, sodium, and potassium chlorides, and ammonium nitrate.

The experiments show that amongst the nitrogenous bodies, only gelatin and urea combine with salicylic acid. And in the case of salts, that only the sodium and ammonium salt of acids having weaker acid properties than salicylic acid, can combine with it. Potassium and calcium salts do not combine at all with salicylic acid.

The author concludes that the power of salicylic acid to prevent fermentation is greater than it was supposed to be by Kolbe and E. Meyer (*J. pr. Chem.* [2], 12, 134). P. P. B.

**Adulteration of Bone Meal with Phosphorite.** By A. v. WACHTEL (*ibid.*, 632).

**Chemical Technological Notes.** By E. DONATH (*Dingl. polyt. J.*, 233, 78—81).—1. *On the Use of Heavy Spar in the Manufacture of Glass*.—An Austrian firm brought out a product which they called "plate glass composition," as a substitute for lime and soda in the manufacture of glass. The authors on analysis declared it to be an intimate mixture of powdered heavy spar and wood charcoal.

Baryta cannot take the place of potash or soda, but by increasing the number of bases in glass, a greater proportion of basic oxides may be introduced, and therefore less alkaline salts would be necessary.

Glass made with barium compounds has a higher specific gravity and brighter lustre than ordinary glass, but their high price stands in the way of their being largely used.

2. *The Composition of Various Kinds of Mirror Glass*.—Analysed by the author.

| Constituents.              | German plate glass. | French. | Rhenish. | So-called German plate-mass. | English. |
|----------------------------|---------------------|---------|----------|------------------------------|----------|
| Silicic acid .....         | 71·45               | 73·64   | 72·22    | 71·02                        | 72·32    |
| Oxides of iron and alumina | 0·51                | 1·40    | 1·53     | 1·22                         | 1·15     |
| Lime .....                 | 11·16               | 14·58   | 15·45    | 9·15                         | 12·64    |
| Magnesia .....             | traces              | 0·30    | traces   | traces                       | traces   |
| Soda .....                 | 16·17               | 10·90   | 10·80    | 18·61                        | 13·18    |

The author concludes that owing chiefly to the proportion of silica and lime, the French glass is the best and the Rhenish next to it, and very nearly as good.

3. *A Test for Free Mineral or Organic Acids.*—Potassium iodide is decomposed with liberation of iodine by potassium dichromate only when there is present free chromic acid, and as the latter is only produced by the action of free mineral acids, this may serve in many ways as a mode of analysis. The author employs carbon bisulphide as the test for free iodine in the solution. W. T.

**Explosion of a Platinum Still used for Concentrating Sulphuric Acid.** By F. KUHLMANN (*Bull. Soc. Chim.* [2], 33, 50—52).—A platinum still, holding about 300 liters, and capable of concentrating 6,000—7,000 kilos. of acid in 24 hours, was stopped for repairs, and all the acid run out except about 40 kilos. Some water was introduced into the still by a syphon, and the mixture gently heated for three or four hours in order to clean the apparatus.

An explosion suddenly occurred which tore the still and still-head into fragments, projecting some to a distance of 30 meters, and dispersed the brick setting on all sides. The explosion was preceded by a slight hissing sound, which warned the workmen just in time for escape.

The author explains the occurrence by the liberation of a large volume of vapour caused by the sudden mixture of the acid and water at a high temperature. Taking the figures of Favre and Silbermann, he shows that enough heat would be produced by the mixture of 40 kilos. of sulphuric acid with water at 18° to generate 18—20 cubic meters of vapour. At 100°, the temperature at which the explosion occurred, the effect would of course be much greater. Experiments on a small scale show that an explosion is always produced when not less than 10 equivalents of water are suddenly mixed with 1 equivalent of acid. J. M. H. M.

**Picking of Grapes.** By C. WEIGELT (*Bied. Centr.*, 1879, 931).—From analytical results, the author entertains favourable opinions of the stripping off of the berries and allowing the skins to ferment, in the production of wine. J. K. C.

**Time of First Drawing of Wine.** By C. WEIGELT and O. SAARE (*Bied. Centr.*, 1879, 930).—The authors arrive at the conclusion that all wines which are obtained from must rich in nitrogen should be drawn early. J. K. C.

**Clearing Action of Spanish Earth.** By C. WEIGELT and O. SAARE (*Bied. Centr.*, 1879, 932).—Experiments on the clearing of wine by means of Spanish earth showed that the quantity of nitrogen in the wine was much diminished by its addition. J. K. C.

**Density of the Mash.** By M. MÄCKER (*Bied. Centr.*, 1879, 619—621).—Comparison is made between the two methods of mashing in alcoholic fermentation, viz., thick and thin mashing, and the advantage which is said to lie with the latter method is not confirmed by the author, who is in favour of a thick mash at a concentration of 22—24° Sac., which appears to be the working limit most favour-



able to fermentation, both with regard to the purity and the amount of alcohol obtained. There is the objection, however, that so concentrated a mash necessitates larger mash-tubs. A. J. C.

**Apparatus for Quick Fermentation.** By HAMMER (*Bied. Centr.*, 1879, 939—940).—By means of this arrangement, of which a full description is given, the percentage of sugar in mash after ten hours' fermentation may be reduced from 18 to 10. J. K. C.

**Malt Comblings a Source of Yeast.** By F. W. MARQUARDT (*Bied. Centr.*, 1880, 69—71).—Dried malt comblings contain a certain amount of protein substances soluble in not too dilute solutions of potato-sugar, and not too dilute molasses, which serve as nourishment to the ferments generated.

Working upon this fact, the author has deduced and perfected a plan, which he has patented, for the preparation of yeast for distillery purposes, and also for the manufacture of compressed yeast for domestic use.

The method employed may be briefly described as the saturation of the comblings with the requisite quantity of potato-sugar or molasses solution (say a solution of the strength 15 per cent. Bolling to every 6—7 parts takes 1 part of comblings), which contains as much actual sugar as comblings employed. It is left for 18 hours, with frequent stirrings; the filaments are then separated, the liquor heated to 20—24° Reaumur (25—30° C.), a little fresh working barm added, and the mixture left in fermenting tubs or other suitable vessels with access of air, the head-barm removed, and the bottoms pressed, with or without the addition of starch according to the use for which it is intended. For extensive distillery purposes, a mash of potatoes, maize, or neutral molasses is at once added instead of the sugar solution.

100 kilos. of comblings are calculated to produce 25—35 kilos. of fine active pressed yeast, and the author believes that 1 kilo. of dry malt comblings contains as much protein matter as 2½ kilos. of dry malt. J. F.

**On Frothy Fermentation.** By E. BAUER (*Bied. Centr.*, 1879, 941—944).—The reason of the frothing which sometimes occurs in the fermentation of potato mash lies, according to the author, in the peculiar organisms developed, and not in the mechanical condition of the liquid. When mash mixed with bottom-yeast, and kept for some time without additional yeast food, is suddenly supplied with yeast nutriment at a temperature which favours top fermentation, frothy decomposition at once sets in. By careful selection of the yeast this may be altogether prevented. J. K. C.

**Surface Fermentation of Potato Mash. Souring of Yeast.** By M. DELBRUCK and others (*Bied. Centr.*, 1879, 621—627).—It is shown that potato spirit and pressed yeast can be advantageously prepared with the same mash, and that there are no grounds of objection against such a process (see also *Bied. Centr.*, 1879, 220; this Journal, 1879, Abst., 843).

The souring of yeast proceeds very actively if the temperature happens to reach 40° R., and if the mash has been made at 50° R. no after cooling of the yeast will arrest it. It is suggested to ensure a uniform acidification by adding soured yeast to the yeast at 40° R., and in order to avoid excess of acidity, a saccharine mash is added to it on the second day after it has been cooled. A. J. C.

**Fermentations produced in preparing Syrups from Beet Juice by Diffusion.** By A. MILLOT and MAQUENNE (*Bull. Soc. Chim.* [2], 32, 611—613).—In treating beetroots (some of which had been frozen) by the diffusion process, the authors noticed a deficiency of about 1 per cent. of sugar in the liquors and residue as compared with that originally in the beet juice. They have traced this loss to fermentations set up during the diffusion, the products of which are carbonic acid, hydrogen, and butyric acid. Ethyl butyrate was also found, but this was probably formed during the analysis. The authors suppose that the acetous fermentation goes on as long as oxygen is present in the diffusion vat, and that when this is exhausted the butyric fermentation commences, of which hydrogen is one of the products. J. M. H. M.

**Proportion of Sugar to the Weight of Beetroots.** By E. FELTZ and H. BRIEM (*Bied. Centr.*, 1880, 59—60).—Feltz made 13 exhaustive laboratory experiments, but on a large scale, using 18 kilos. in each, in order to determine the relation between the weights of the roots and the sugar contained in their juice. The general results arrived at are that the richness of the juice in the sugar is the greater as the juice is thicker, that the smaller sized roots generally yield the thickest and consequently the richest juice, although it cannot be given as an absolutely fixed rule that the smaller the root the greater the proportion of sugar, but it is sufficiently proved for technical purposes. The most satisfactory results were obtained from roots weighing 200—300 grams; those from 300—400 were but slightly inferior; above that weight, however, the percentage of sugar rapidly declined. J. F.

**Analyses of Sugar.** By J. MOSER and others (*Bied. Centr.*, 1879, 926).—Very many samples of raw sugar from various sources have been analysed by means of Sachsse's modification of Knapp's method. The solution used consisted of 18 grams mercuric iodide, 25 potassium iodide, and 80 potash, dissolved up to a liter. 40 c.c. of this solution correspond to 0.1342 gram of dextrose. J. K. C.

**Bassia Longifolia.** By A. RICHÉ and A. REMONT (*J. Pharm. Chim.* [5], 1, 215—218).—*Bassia longifolia*, a tree of the order *Lapetææ*, contains a large amount of sugar. The bark and leaves are used in medicine, and the seeds contain a fatty substance known as "butter of Allipa." The flowers when dry have much the appearance of dried raisins, and contain about 61 per cent. of fermentable sugar and about 8.5 per cent. of crystallisable sugar. The fatty substance melts at a higher temperature than other similar bodies, and therefore might be used in the manufacture of tapers. L. T. O'S.

**Valuation of Raw Sugar.** By K. STAMMER (*Bied. Centr.*, 1879, 929).—The author thinks that 5 is too high a multiple of the quantity of salts contained in raw sugar to be used in valuation, and considers that only 3·5 times the percentage of salts present should be subtracted from the total quantity of sugar present in order to give the possible yield of refined sugar.  
J. K. C.

**Suint.** By E. SCHULZE and J. BARBIERI (*Bied. Centr.*, 1879, 596—598).—The authors have investigated a peculiar kind of sheep sweat of a "pitch-like" character, containing a large quantity of fatty matter, of which 84 per cent. is described as being difficultly soluble in alcohol. The portion soluble in alcohol differed from that of ordinary suint in containing no cholesterin in the free state, and in giving only a very small quantity even by saponification. In other respects there was no essential difference in the nature of this kind of suint and the ordinary sheep sweat as described in Schulze's previous papers (this Journal, 1878, 920 and 1219; 1874, 1079). Expressed on the raw wool, the amount of fatty matter was in these cases found to be 34·19 per cent. (m. p. 35·5°), 35·16 (m. p. 37°), and 36·31 (m. p. 44°), and the amount soluble in water 9·76, 13·77, and 12·15 per cent. respectively, whilst ordinary wool, in two examples quoted amongst others, contained 7·17 and 14·66 per cent. fatty matter, with 21·13 and 21·83 per cent. soluble in water. The aqueous solution contained no potash soap, and this peculiarity, together with the large amount of fatty matter, explains the fact that this kind of wool is so imperfectly cleansed by water. The ether extract of the wool consisted of pure fatty matter, whilst that of ordinary wool always contains potassium oleate. In addition to inorganic compounds, the aqueous solution is said to contain an organic acid, the nature of which has not been examined.  
A. J. C.

**Destructive Action of Wood on Salicylic Acid.** By H. KOLBE (*J. pr. Chem.* [2], 443—447).—Water, to which salicylic acid has been added in proportion of 0·1 gram to the liter, may be kept for a year in a glass vessel and will then be found to be quite fresh; but if double the amount of the acid is added to water in a wooden cask or in a glass vessel containing wood, the water becomes bad, and the acid totally disappears; it cannot be detected either in the water or the wood. The same result was obtained on substituting wine for water.

In what way the acid is destroyed is an open question.

G. T. A.

**Analyses of Milk.** By J. MOSER and F. SOXHLET (*Bied. Centr.*, 1879, 934—937).—In the samples of condensed milk analysed, the percentage of water varied from 24 to 30, fat from 7·5 to 11, and casein from 9 to 11. The sp. gr. of goat's milk varied from 1·027 to 1·045. Mare's milk was found to contain 92 per cent. of water, and about 1·5 per cent. of casein.  
J. K. C.

## General and Physical Chemistry.

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**Effect of Light on Chemical Compounds.** By T. P. BLUNT (*Analyst*, 1880, 79—81).—The author finds that solutions of certain compounds when exposed to the light undergo decomposition. A solution of oxalic acid may be kept for any length of time in the dark, whereas if exposed to the light it rapidly undergoes decomposition; some solutions exposed to the light for six months in test-tubes stoppered with cotton wool, lost all traces of acidity. Dilute solutions of alkaline oxalates undergo similar oxidation, notably ammonium oxalate.

In the dark, dilute permanganate solution may be kept for months unchanged.

From experiments with potassium iodide, the author concludes that the oxidation is due to the effect of light alone, without the intervention of any acid.

Ferrous iodide, however, requires exposure to the brightest possible light to prevent decomposition. L. T. O'S.

**A New Voltaic Condenser.** By — D'ARSONVAL (*Compt. rend.*, 90, 166—167).—The action of secondary piles, such as those devised by Planté, is very energetic for a short time, but not lasting. An attempt was therefore made to discover the causes which limit the condensing power of the lead-plate couple, and if possible to rectify them. The gaseous state of the oxidisable metal (hydrogen) unquestionably limits the action, and this soon attains a maximum, which it is impossible to exceed, the lead plate becoming covered with a layer of dioxide which protects the metal from further oxidation. A cell was therefore devised in which a zinc plate was used in connection with a carbon one, the latter being surrounded with very fine leaden shot (dust-shot) in order to increase enormously the surface of the lead, and the whole was excited with a solution of zinc sulphate. On passing a current from the carbon to the zinc through a couple thus constructed, the zinc salt is decomposed, and the metal deposited on the zinc plate, the oxygen forms lead dioxide, whilst the sulphuric acid remains free; the deposit of oxidisable metal is thus unlimited, and the oxygen can be accumulated in very large quantity. With a couple containing only 1 kilo. of shot, the author succeeded in working a Deprez electromotor for four hours.

In practice, the zinc plate may be replaced by a mercury pole; the electromotive force of such a couple was found to be 2.1 volts. The lead plate also may be replaced by several other substances, but nothing else seemed to give such satisfactory results. J. W.

**Determination of High Temperatures.** By H. ST. CLAIRE DEVILLE and L. TROOST (*Compt. rend.*, 90, 727—730).—The thermometric apparatus consists of a cylindrical reservoir of porcelain, of at least 50 c.c. capacity, furnished with a capillary porcelain tube about

0.3 mm. long, to which is attached a three-way stopcock communicating with the air, and, by means of an almost capillary lead tube, with a Sprengel pump. The thermometer is placed in a refractory glazed earthen tube, packed with asbestos and heated in a furnace fed with petroleum. The temperature of this furnace can be adjusted by regulating the flow of oil by means of a sensitive stopcock. When the temperature has become constant, communication between the reservoir, the air, and the pump is cut off. The tube connecting the thermometer to the pump is first rendered vacuous, the stopcock is then opened, and the gas (nitrogen) contained in the thermometer is pumped out into a graduated tube, and its volume determined with the greatest possible accuracy. The necessary correction for the capillary portion of the thermometer is ascertained by determining the volume of gas in a tube of the same length and diameter, placed at its side, and which the authors term a compensator.

C. H. B.

**Heat of Formation of the Oxides of Nitrogen.** By BERTHELOT (*Compt. rend.*, 90, 779—784).—The author has determined the heat of formation of nitric oxide by exploding cyanogen and ethylene respectively, first with this gas and afterwards with oxygen, and measuring the amount of heat evolved in each case. The heat of formation of nitrous oxide was determined by exploding it with carbon monoxide. The results, together with those of experiments on the heat of formation of other nitrogen compounds are given in the following tables:—

## I.

Cals.

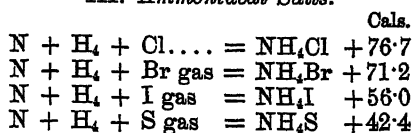
|                                 |                |  |
|---------------------------------|----------------|--|
| $N_2 + O$ .....                 | $= N_2O$ gas   | -20.6                                      |
| $N_2 + O_2$ .....               | $= N_2O_2$ gas | -43.2                                      |
| $N_2 + O_3$ .....               | $= N_2O_3$ gas | -22.2 dis. - 8.4                           |
| $N_2 + O_4$ .....               | $= N_2O_4$ gas | - 5.2 liq. + 3.4                           |
| $N_2 + O_5$ .....               | $= N_2O_5$ gas | - 1.2 liq. + 3.6 sol. + 11.8 dis. + 28.6   |
| $\frac{1}{2}(N_2 + O_5 + H_2O)$ | $= HNO_3$ gas  | - 0.1 liq. + 7.1 sol. + 7.7 dis. + 14.3    |
| $N + O_3 + H..$                 | $= HNO_3$ gas  | + 34.0 liq. + 41.6 sol. + 42.2 dis. + 48.8 |
| $N + H_3$ .....                 | $= NH_3$ gas   | + 12.2 dis. + 21.0                         |
| $N + H_3 + O..$                 | $= NH_3O$ dis. | + 19.0                                     |
| $O + N$ .....                   | $= CN$ gas     | - 37.3                                     |

## II. Nitrates.

Cals.

|                         |                     |         |
|-------------------------|---------------------|---------|
| $N + O_3 + K$ .....     | $= KNO_3$ .....     | + 118.7 |
| $N + O_3 + Na$ ....     | $= NaNO_3$ ....     | + 110.6 |
| $N_2 + O_3 + H_4$ ....  | $= NH_4NO_3$ ....   | + 87.9  |
| $N_2 + O_3 + Sr$ ....   | $= Sr_2NO_3$ ....   | + 219.6 |
| $N_2 + O_3 + Ca$ ....   | $= Ca_2NO_3$ ....   | + 202.4 |
| $N_2 + O_3 + Pb$ ....   | $= Pb_2NO_3$ ....   | + 105.6 |
| $N + O_3 + Ag$ ....     | $= AgNO_3$ ....     | + 28.7  |
| $N + O_3 + C_2 + H_5$   | $= C_2H_5NO_3$ .... | + 52.4  |
| $N_3 + O_3 + C_3 + H_5$ | $=$ nitroglycerine  | + 96.4  |
| $C_6 + H_5 + N + O_3$   | $=$ nitrobenzene    | + 4.2   |
| $C_6 + H_5 + N_2 + O_4$ | $=$ dinitrobenzene  | + 12.7  |

## III. Ammoniacal Salts.



C. H. B.

**Thermochemical Study of Sulphides of the Earth-metals.** By P. SABATIER (*Compt. rend.*, 90, 819—821).—*Magnesium sulphide*, obtained by the action of carbon bisulphide on the oxide at a red heat. The solution of one equivalent in hydrochloric acid causes development of heat = +21.8 cal. at 13°, hence the heat of formation of  $MgS$  (56 grams) = +73.6 cal. The conversion of  $MgS$  into  $Mg(HO)_2$  by the action of water develops +10.4 cal.

*Aluminium sulphide*, prepared by heating the metal to redness in the vapour of sulphur. When one equivalent is decomposed by water at 12°, +74.0 cal. are developed, which gives the heat of formation of  $Al_2S_3$  (150.8 grams) = +124.4 cal.

*Silicon sulphide*, obtained in the form of long silky needles by the action of carbon bisulphide on silica heated to redness. The decomposition of one equivalent by water causes development of heat = +38.5 cal. at 9.5°, which gives the heat of formation of  $SiS_2$  (92 grams) = +40.4 cal., a number much lower than the heat of formation of the corresponding oxide.

C. H. B.

**Freezing Point of Alcoholic Liquids.** By F. M. RAOULF (*Compt. rend.*, 90, 865—868).—Mixtures of alcohol and water when subjected to low temperatures congeal but never completely solidify. That which solidifies consists of plates of pure ice, and can be freed from alcohol by simple mechanical means. The temperatures at which congelation begins in mixtures of alcohol and water containing different percentages of the former, are given in the following table, which may be used for the determination of the strength of such mixtures:—

| Temperature. | Vol. alcohol<br>per cent. | Temperature. | Vol. alcohol<br>per cent. |
|--------------|---------------------------|--------------|---------------------------|
| —0.0°        | 0.0                       | —9.0°        | 21.9                      |
| —0.5         | 1.6                       | —10.0        | 23.3                      |
| —1.0         | 3.2                       | —12.0        | 26.4                      |
| —1.5         | 4.8                       | —14.0        | 29.1                      |
| —2.0         | 6.3                       | —16.0        | 31.3                      |
| —2.5         | 7.8                       | —18.0        | 33.8                      |
| —3.0         | 9.2                       | —20.0        | 36.1                      |
| —3.5         | 10.6                      | —22.0        | 38.3                      |
| —4.0         | 11.8                      | —24.0        | 40.0                      |
| —4.5         | 13.1                      | —26.0        | 41.6                      |
| —5.0         | 14.2                      | —28.0        | 43.7                      |
| —6.0         | 16.4                      | —30.0        | 46.2                      |
| —7.0         | 18.7                      | —32.0        | 47.9                      |
| —8.0         | 20.4                      |              |                           |

In solutions containing from 0 gram to 10 grams of alcohol to 100 grams of water, the addition of 1 gram of alcohol lowers the point of congelation by  $0.377^{\circ}$ , and the distance of this point below zero is proportional to the weight of alcohol dissolved in a constant weight of water. The alcohol behaves like anhydrous salts, and therefore probably exists in the liquid uncombined with water. In solutions containing 24 to 51 grams of alcohol to 100 grams of water, the addition of 1 gram of alcohol lowers the congelation point  $0.528^{\circ}$ , but the total distance of this point below  $0^{\circ}$  bears no relation to the amount of alcohol in the liquid. This fact indicates that the alcohol dissolves in the hydrated condition. Applying Rudorff's method of calculation, it is found that this hydrate has the composition  $C_2H_5O.H_2O$ .

The following table gives the points of congelation of various fermented liquors, compared with those of aqueous solutions of alcohol of the same strength:—

|                          | Per cent.<br>alcohol. | Congelation<br>point. | Cong. point.<br>Aqueous alcohol. |
|--------------------------|-----------------------|-----------------------|----------------------------------|
| Cider .....              | 4.8                   | — $2.0^{\circ}$       | — $1.5^{\circ}$                  |
| Beer .....               | 6.3                   | — $2.8$               | — $2.0$                          |
| Vin rouge ordinaire .... | 6.8                   | — $2.7$               | — $2.2$                          |
| Vin blanc ordinaire .... | 7.0                   | — $3.0$               | — $2.3$                          |
| Beaugolais .....         | 10.3                  | — $4.4$               | — $3.4$                          |
| Red Bordeaux .....       | 11.8                  | — $5.2$               | — $4.0$                          |
| Red Burgundy .....       | 13.1                  | — $5.7$               | — $4.5$                          |
| Red Roussillon .....     | 15.2                  | — $6.9$               | — $5.5$                          |
| Marsala .....            | 20.7                  | — $10.1$              | — $8.1$                          |

Fermented liquors require a lower temperature for congelation than the corresponding aqueous solutions of alcohol, and the difference is greater the greater the proportion of alcohol; it is about  $0.1^{\circ}$  for each percentage of that liquid. That which solidifies is pure ice, and by removing this as fast as it is formed, the alcohol in the liquid may be gradually concentrated.

C. H. B.

**Some Properties of Mixtures of Methyl Cyanide with Ethyl and Methyl Alcohols.** By C. VINCENT and DELACHANAL (*Compt. rend.*, 90, 747—750).—The following table gives the boiling points and specific gravities of various mixtures of ethyl alcohol and pure

| Alcohol. | Methyl cyanide. | Sp. gr. | Contraction. | B. p.          |
|----------|-----------------|---------|--------------|----------------|
| 0        | 100             | 0.8052  | 0.0          | $81.6^{\circ}$ |
| 10       | 90              | 0.8059  | 0.00007      | 76.8           |
| 20       | 80              | 0.8067  | 0.00017      | 74.8           |
| 30       | 70              | 0.8075  | 0.00029      | 73.8           |
| 40       | 60              | 0.8083  | 0.00046      | 73.2           |
| 50       | 50              | 0.8092  | 0.00071      | 72.7           |
| 60       | 40              | 0.8102  | 0.00111      | 72.7           |
| 70       | 30              | 0.8114  | 0.00177      | 73.2           |
| 80       | 20              | 0.8127  | 0.00251      | 74.1           |
| 90       | 10              | 0.8130  | 0.00211      | 75.4           |
| 95       | 5               | 0.8130  | 0.00138      | 75.4           |
| 100      | 0               | 0.8120  | 0.0          | 78.4           |

methyl cyanide obtained from coal-tar naphtha (this Journal, 34, 392, and boiling at 81.6°.

The boiling points of these mixtures are lower than that of either constituent. When subjected to fractional distillation, a distillate is obtained which at first contains 56 per cent. of alcohol, and afterwards a higher or lower percentage according as the mixture in the retort contains more or less than 56 per cent. The methyl cyanide may be separated from the alcohol by repeated treatment with calcium chloride, and finally with phosphoric anhydride. In this way, it may be obtained in large quantities in a state of purity from coal-tar naphtha.

The following table gives the results obtained with mixtures of methyl cyanide with pure anhydrous methyl alcohol, boiling at 64.8°:—

| Alcohol. | Cyanide. | Sp. gr. | Contraction. | B. p. |
|----------|----------|---------|--------------|-------|
| 0        | 100      | 0.8052  | 0.0          | 81.6° |
| 10       | 90       | 0.8063  | 0.00076      | 74.0  |
| 20       | 80       | 0.8073  | 0.00148      | 69.2  |
| 30       | 70       | 0.8083  | 0.00218      | 67.1  |
| 40       | 60       | 0.8093  | 0.00278      | 65.7  |
| 50       | 50       | 0.8102  | 0.00332      | 64.8  |
| 60       | 40       | 0.8110  | 0.00378      | 64.2  |
| 70       | 30       | 0.8115  | 0.00384      | 63.8  |
| 80       | 20       | 0.8115  | 0.00318      | 63.7  |
| 90       | 10       | 0.8109  | 0.00192      | 64.0  |
| 100      | 0        | 0.8098  | 0.0          | 64.8  |

C. H. B.

#### Relation between Molecular Weight and Density of Gases.

By A. NAUMANN (*Ber.*, 13, 468—470).—A reply to Schmidt's assumption (*Ann. Phys. Chem.* [2], 6, 612, this vol., p. 87), that  $V$ , i.e., the molecular weight of gas divided by its density referred to air as unity, equals 28.8384 instead of 28.88.

W. C. W.

**Absorption of Gases by Liquids.** By A. NACCARI and S. PAGLIANI (*Gazzetta*, 10, 119—120).—From the experimental results obtained by Bunsen and others the authors show—

1. That the absorption of carbonic anhydride by water follows Henry's law for pressures of from one to four atmospheres.

2. That scarcely any experiments have been made at pressures less than one atmosphere.

3. That gases which are absorbed by water to a considerable extent vary from Henry's law when the pressure is low.

On making experimental determinations, however, of the solubility of carbonic anhydride in water at temperatures between 17° and 27°, and at pressures from 257.7 to 663.6 mm., they found that the results obtained approximated closely to those calculated from Henry's law. The coefficient of absorption of carbonic anhydride by water between 17° and 27°, as deduced from the author's experiments may be represented by the formula—

$$\alpha = 1.5062 - 0.036511 t + 0.0002917 t^2,$$



which differs somewhat from that given by Bunsen for temperatures between  $0^{\circ}$  and  $20^{\circ}$ .

A table is given of the observed and calculated values for different temperatures, reduced to 760 mm. pressure, on the supposition of the truth of Henry's law. C. E. G.

**Determination of High Temperatures.** By H. ST. CLAIRE DEVILLE and L. TROOST (*Compt. rend.*, 90, 773—778).—The authors give the results of experiments made some years ago to determine the boiling point of commercial zinc. The air-thermometer employed was constructed of Bayeux porcelain, glazed within and without, and protected by screens to prevent loss by radiation. Several kilograms of zinc were distilled at each operation, and care was taken to prevent the overheating of the vessel in which the thermometer was placed. The numbers obtained were  $916$ — $925^{\circ}$ , when the thermometer was filled with hydrogen,  $929$ — $954^{\circ}$ , with dry air, and  $1067$ — $1079^{\circ}$  when carbonic anhydride was the gas employed, indicating dissociation of this gas. C. H. B.

**Researches on Diffusion.** By L. JOULIN (*Compt. rend.*, 90, 741—744).—The author has studied the influence of pressure, ranging from a few centimeters of mercury to four atmospheres, and temperature between  $0^{\circ}$  and  $100^{\circ}$ , on the condensation of gases by porous solids, the solution of gases in liquids, and the equilibrium between the condensed or dissolved gases and the surrounding atmosphere, with the following results:—(1.) *Wood Charcoal.*—The amount by weight of dry oxygen, nitrogen, and hydrogen condensed, is directly proportional to the pressure and inversely proportional to the temperature. The time necessary for saturation is too small to admit of measurement. With carbonic anhydride, the amount condensed increases more rapidly than the pressure up to 300 mm., and decreases more rapidly than the temperature rises, between  $0^{\circ}$  and  $100^{\circ}$ , but above these limits it obeys the same law as the other three gases. The time necessary for saturation increases with the pressure, and decreases with a rise of temperature. The condensation of gaseous mixtures is slower than that of each constituent, and the amount of each gas absorbed bears no relation to the proportion in which it exists in the mixture. The quantity of gas required to replace a given volume of carbonic anhydride is much less for nitrogen and hydrogen than for oxygen. Air behaves like a mixture of its constituents. The time necessary for the establishment of equilibrium varies with the nature of the atmosphere, being very short for hydrogen, longer for nitrogen, and still longer for oxygen. When the gases are saturated with vapour, the phenomena are of the same order, but differ in degree. The amount of carbonic anhydride condensed, when saturated with aqueous vapour, is one-half, and when saturated with vapour of alcohol, one-fifth that of the dry gas. (2.) *Charcoal saturated with liquid.*—When the liquid is water, the absorptions are almost the same as with dry charcoal; but with carbon bisulphide the amount of gas condensed is smaller, and still smaller with alcohol. The author has experimented with other porous substances, such as spongy platinum

and palladium, but as yet without any definite results. At ordinary temperatures and pressures, different specimens of earth absorb notable quantities of the gases in the air, the oxygen being absorbed to twice the amount of the nitrogen.

C. H. B.

## Inorganic Chemistry.

**Sulphides and Selenides of Chromium.** By H. MOISSAN (*Compt. rend.*, 90, 817—819).—*Chromium sesquisulphide*,  $\text{Cr}_2\text{S}_3$ .—Obtained as a brownish-black amorphous powder by passing dry hydrogen sulphide over heated, but not calcined, sesquioxide. It is but slightly attacked by acids, with the exception of nitric acid and *aqua regia*. When heated in chlorine gas, it is converted with incandescence into chromic chloride. On heating it in the air, the sesquioxide is formed; but if it be heated in a closed vessel, a portion of the sulphur is given off in the free state. By the action of hydrogen sulphide on chromic chloride, this compound is obtained in black brilliant plates, which retain the form of the chloride.

*Chromium monosulphide*,  $\text{CrS}$ .—A black powder, attacked with difficulty by acids, but readily converted into chromic chloride by chlorine, obtained by heating the preceding compound in hydrogen. When heated in the air, it is converted into the sesquioxide, but does not lose sulphur when heated in a closed vessel. By heating chromous chloride at  $440^\circ$  in hydrogen sulphide, the monosulphide is obtained as a greyish-black substance, retaining the micaceous appearance of the chloride.

*Chromium sesquiselenide*,  $\text{Cr}_2\text{Se}_3$ , is a black powder, obtained by the action of hydrogen selenide on chromic chloride, or by heating the sesquioxide in selenium vapour. It is very slightly attacked by acids, and readily converted into a beautiful green-coloured sesquioxide when heated in the air. Heated out of contact with air, it loses a portion of its selenium.

*Chromium monoselenide*,  $\text{CrSe}$ .—Obtained by heating the preceding compound in a current of hydrogen, or by the action of hydrogen selenide on chromous chloride. It is easily converted into the sesquioxide on ignition, and is readily attacked by chlorine.

C. H. B.

**A New Property of Vanadates.** By P. HAUTEFVILLE (*Compt. rend.*, 90, 744—747).—The acid vanadates of potassium, sodium, and lithium, have the property of “spitting,” like metallic silver, when cooled after fusion in presence of air. The gas thus given off is oxygen, and the amount absorbed by a given quantity of vanadate is constant; lithium bivanadate, for example, when fused at a dull-red heat, absorbs nearly eight times its own volume of oxygen, which is again given off at about  $600^\circ$  during the process of cooling. The following table shows the volume of oxygen given off when an amount of vanadate containing 1 gram of vanadic acid is fused in a vacuum:—

| Product.             | c.c. | Product.              | c.c. | Product.              | c.c. |
|----------------------|------|-----------------------|------|-----------------------|------|
| $2V_2O_5.K_2O \dots$ | 0.4  | $2V_2O_5.Na_2O \dots$ | 3.8  | $2V_2O_5.Li_2O \dots$ | 3.3  |
| $3V_2O_5.K_2O \dots$ | 0.5  | $3V_2O_5.Na_2O \dots$ | 5.0  | $3V_2O_5.Li_2O \dots$ | 3.7  |
| $4V_2O_5.K_2O \dots$ | 2.7  |                       |      |                       |      |
| $5V_2O_5.K_2O \dots$ | 3.4  |                       |      |                       |      |

It will be seen that the volume of gas disengaged increases as the relative proportion of base diminishes.

When vanadic acid is acted on by an alkaline carbonate, oxygen is also evolved. The following table shows the amount of gas given off when 1 gram of vanadic acid is acted on in a vacuum by alkaline carbonates:—

| Product.             | c.c. | Product.              | c.c. | Product.              | c.c. |
|----------------------|------|-----------------------|------|-----------------------|------|
| $V_2O_5.K_2O \dots$  | 0.0  | $V_2O_5.Na_2O \dots$  | 0.4  | $V_2O_5.Li_2O \dots$  | 2.5  |
| $2V_2O_5.K_2O \dots$ | 0.7  | $2V_2O_5.Na_2O \dots$ | 4.0  | $2V_2O_5.Li_2O \dots$ | 4.7  |
| $3V_2O_5.K_2O \dots$ | 1.5  | $3V_2O_5.Na_2O \dots$ | 5.4  | $3V_2O_5.Li_2O \dots$ | 5.8  |
| $4V_2O_5.K_2O \dots$ | 3.3  |                       |      |                       |      |
| $5V_2O_5.K_2O \dots$ | 4.8  |                       |      |                       |      |

The volume of oxygen absorbed by a crystalline vanadate, when fused in presence of air, serves as an indication of the relative proportions in which a vanadate and vanadic acid may be fused together without combination taking place. These observations render it advisable to redetermine the atomic weight of vanadium, since this quantity has been fixed by ascertaining the loss of weight which vanadic anhydride experiences when passing to the state of trioxide.

C. H. B.

**Composition and Analysis of the Binoxide of Manganese recovered in the Weldon Process.** By G. LUNGE (*Dingl. polyt. J.*, 235, 300—311).—Post (*Ber.*, 12, 1454 and 1537) publishes some researches on Weldon-mud, which seem to show that Weldon's theory of the "manganites," *i.e.*, saline compounds of  $MnO_2$  with bases, which he applies as a definition of his process, is not only unfounded, but that the methods used in works for the analysis of Weldon-mud must be totally wrong. Post states (p. 1539) that he has obtained a wide difference between the ferrous sulphate method as laid down by the author and Bunsen's iodine method. The present paper is devoted entirely to this statement, and in a very complete series of experiments the author discusses this question, and proves without doubt that the methods formerly described by him for analysing Weldon-mud are perfectly trustworthy.

Post in his researches entirely ignores the existence of a base, and regards the Weldon-mud as a mechanical mixture of  $MnO_2$  with  $MnO$  and a small proportion of lime, magnesia, and ferric oxide, the former present probably as carbonates, but the total sum not sufficient to form Weldon's "acid manganite" ( $RO_2MnO_2$ ).

The author refers to this assumption very briefly, and mentions that Post did not analyse Weldon-mud itself, but a product obtained by a very troublesome process of washing (100 times with 40 times its weight of water), which had probably been altered by this treatment

to a considerable extent. Various circumstances undoubtedly show that this binoxide of manganese is a salt of manganous oxide with manganic acid or permanganic acid, *i.e.*,  $\text{MnO}$ ,  $\text{MnO}_2$  or  $3\text{MnO}$ ,  $\text{Mn}_2\text{O}_7$ . In this case Weldon's manganous salts would represent basic manganates or "permanganates," *i.e.*,  $\text{CaO}$ ,  $2\text{MnO}_2$  would be  $\text{CaO}$ ,  $\text{MnO}$ ,  $\text{MnO}_2$ , &c.

D. B.

## Mineralogical Chemistry.

**Step-like and Skeleton Growth of some Regular Crystals.** By F. SCHARFF (*Jahrb. f. Min.*, 1878, 953—954).—The development of the various crystals of the regular system is dependent on a varying disposition of the building material, and the proof of this is seen in the common occurrence of striations in different directions, of polyhedral elevations on the faces, and of hollow faces. These peculiarities are brought about by the influence exerted on the crystals during their growth by the working one into the other of the various systems of "directions of activity" (*thätigkeitsrichtungen*), thus causing the formation of edges, faces, and cleavage directions. These actions of the directions of activity can be retarded or interfered with externally, so that the formation of one or other face is promoted or induced. Cubical and octohedral forms are most easily produced. On the faces of the cube, there is often observed a quadruple concentration in the polyhedral elevation; whilst on the faces of the octohedron only a triple concentration is observed. In iron pyrites, the pentagon-dodecahedron takes up an intermediate position between these two concentrations; for instance, the horizontal striation on some of the faces points to cubical structure, whilst the inclined or vertical striation points to octohedral structure. Hemihedral formation appears to be due to the partial coincidence of two different systems of "directions of activity" in one place. The complete crystal is built up exactly similar to the form of its minutest particle. The development of secondary faces is generally intimated on the polyhedral elevations observed on the neighbouring faces. In a similar manner the hollow faces remaining behind are intimately connected in form with the neighbouring faces, and they can easily be distinguished from "etch-figures." Intersecting or reticulated striation is caused by the intersecting of systems of "directions of activity," good examples of such a striation being often observed on fluorspar crystals, resulting occasionally in the formation of a tetrakis-hexahedron and at other times in the formation of a hexakis-octohedron.

C. A. B.

**Sensitiveness of Alum-crystals to Variations in the Strength of their Mother-liquor.** By F. KLOCKE (*Jahrb. f. Min.*, 1878, 958—959).—The author made some experiments in order to ascertain the correctness of the law of Lecoq de Boisbaudran, *viz.*: "A crystal face can remain unchanged—that is, neither increase nor decrease in size—

in a fluid whose degree of concentration changes within determinable limits." In order to test the accuracy of this statement, Klocke placed alum crystals in a saturated solution of alum and examined them microscopically, in order to ascertain whether any variation in the concentration of the solution would produce "etch-figures" on the crystals. The result proved the inaccuracy of the above-mentioned law, as "etch-figures" were easily and distinctly produced; the so-called inertia of the crystal faces therefore is not a fact. An apparent inertia of the crystals can be brought about by layers of liquid (differing in degrees of concentration, owing to the oscillations of temperature) being present in the solution, but the crystal dissolves in an adjacent non-saturated layer until the resulting solution about the crystal is saturated, or it grows in an adjacent saturated solution. A crystal which is rounded off at one end sometimes exhibits sharply-defined faces at the other end; and if the whole crystal then grows further, new faces grow on the rounded end which do not occur at the other end, thus producing an apparent hemimorphism. C. A. B.

**Chemical Composition of the Pitchblende (Uraninite) from Branchville, Conn., U.S.** By W. J. COMSTOCK (*Amer. J. Sci.* [3], 19, 220).—The crystals, which were very distinct, were octohedral, modified by the planes of the dodecahedron and cube. Their sp gr. is 9.22—9.28, and their composition as follows:—

| U.    | Pb.  | Fe.  | O.    | H <sub>2</sub> O. |
|-------|------|------|-------|-------------------|
| 81.50 | 3.97 | 0.40 | 13.47 | 0.88 = 100.22     |

The formula indicated by this composition is  $3R^VO_2 + 2R^VO_3$ , in which  $R^V$  represents tetrad uranium, replaceable by two atoms of lead or iron and  $R^VI$ , hexad uranium. C. W. W.

**Crystallography of Calcite.** By IRBY (*Jahrb. f. Min.*, 1878, 952—953).—The author continued the investigations commenced by Hessenberg, and directed his attention particularly to the inner constitution of calcite crystals, and from the results obtained, was of opinion that Hany's theory was more worthy of the consideration which German mineralogists had hitherto declined to bestow upon it. Irby examined the development of the crystal forms from the primary rhombohedron, and also the combinations of the different forms with each other. He accounts for the great rarity of the primary rhombohedron occurring independently, by the fact that foreign substances present in the solution of calcium carbonate exert a retarding influence on the independent formation of the primary rhombohedron, and conduce to the simultaneous occurrence of other forms. Irby gives tables of all the rhombohedrons and scalenohedrons known (49 of the former and 100 of the latter), with their interfacial angles.

C. A. B.

**Chemical Composition of Amblygonite.** By S. L. PENFIELD (*Amer. J. Sci.* [3], 18, 295).—In describing triploidite, Brush and Dana (*Amer. J. Sci.* [3], 16, 42; this Journal, 36, 20) showed that the hydroxyl-group which enters into its constitutional formula

must play the same part as the fluorine in the allied species, wagnerite and triplite. In this paper, the author shows that the hydroxyl in amblygonite also replaces fluorine. This conclusion is deduced from a very large number of analyses, the particulars of which are given in the original paper. For more easy comparison, the ratio for phosphoric acid, alumina, alkalis (sodium and lithium oxides), and of hydroxyl and fluorine, are given below, as also the localities from which the minerals were obtained :—

|                              | $P_2O_5$ . | $Al_2O_3$ . | $Na_2O.Li_2O$ . | OH.F. |
|------------------------------|------------|-------------|-----------------|-------|
| I. Penig, Saxony.....        | 1.00       | 0.96        | 0.98            | 1.16  |
| II. Montebbras, France (A)   | 1.00       | 0.97        | 0.98            | 1.17  |
| III. Auburn, Maine .....     | 1.00       | 0.96        | 0.97            | 1.06  |
| IV. Hebron, Maine (A) ..     | 1.00       | 0.97        | 0.95            | 1.13  |
| V. Paris, Maine .....        | 1.00       | 0.96        | 0.97            | 1.17  |
| VI. Hebron, Maine (B) ..     | 1.00       | 0.98        | 0.95            | 1.27  |
| VII. Branchville, Conn.....  | 1.00       | 0.97        | 0.96            | 1.09  |
| VIII. Montebbras, France (B) | 1.00       | 0.96        | 0.96            | 1.21  |

It will be seen that all these ratios approach very nearly 1 : 1 : 1 : 1 ; therefore the author proposes the formula  $Al_2P_2O_8 + 2R(OH,F)$  or  $3Al_2P_2O_8 \left. \vphantom{Al_2P_2O_8} \right\} + \left. \vphantom{Al_2P_2O_8} \right\} \begin{matrix} Al_2(OH,F)_6 \\ 2R_2(OH,F) \end{matrix}$  as the true formula for all varieties of the mineral.

To explain the fact that the (OH,F) is in every case too high, whilst the alkalis and alumina are constantly, although slightly, too low, he supposes either that a small quantity of accidental water is always present, or that some of the water is basic. C. W. W.

**Analyses of some American Tantalates.** By W. J. COMSTOCK (*Amer. J. Sci.* [3], 19, 131).—Of these minerals, the first came from Yancey Co., N.C. ; it was a massive piece, of sp. gr. 6.88 ; the second was from Northfield, Mass., a fragment of a large crystal having the angles of ordinary columbite ; sp. gr. 6.84. No. III was from Branchville, Conn. ; slightly translucent in thin fragments, and giving a brownish-grey powder ; sp. gr. 6.59.

|        | $Ta_2O_5$ . | $Nb_2O_5$ . | FeO.  | MnO.  | MgO. | CaO.         |
|--------|-------------|-------------|-------|-------|------|--------------|
| I ..   | 59.92       | 23.63       | 12.86 | 3.06  | 0.34 | — = 99.81    |
| II ..  | 56.90       | 26.81       | 10.05 | 5.88  | —    | — = 99.64    |
| III .. | 52.29       | 30.16       | 0.43  | 15.58 | —    | 0.37 = 98.83 |

These all agree with the formula  $(Fe,Mn)(Ta,Nb)_2O_6$ .

C. W. W.

**Two New Silicotitanates of Sodium.** By P. HAUTEFVILLE (*Compt. rend.*, 90, 868—870).—By heating one equivalent of sodium titanate to bright redness with sodium tungstate, and heating this product to dull redness with two equivalents of silica, two definite compounds are produced. One of these,  $4SiO_2.5TiO_3.2Na_2O$ , is obtained in nodules formed of radiating fibres, or in flat finely channelled prisms. The faces of the prisms and the sections of the nodules have a brilliant silky lustre. The crystals are always opalescent, and strongly birefractive ; they are very fragile, but scratch glass and

resist the action of acids which attack the native silicotitanate of calcium.

The other compound,  $3\text{SiO}_2 \cdot 2\text{TiO}_2 \cdot \text{Na}_2\text{O}$ , forms colourless, transparent, very refractive orthorhombic prisms, isolated or united in druses. The faces  $a'$  and  $e'$  are found on all the crystals, but are often very small. The cleavage is parallel to the faces of a prism of  $91^\circ$ , and the ratio,  $b$  to  $h$ , = 1 : 0.544. Optical examination proves that the crystals belong to the orthorhombic, and not to the quadratic system.

By replacing tungstates by vanadates it will probably be possible to obtain compounds between those described and sphene. The silicotitanates differ from the natural silicates in fusing to a colourless limpid bead before the blowpipe. When fused, they devitrify very rapidly with separation of rutile.

C. H. B.

**Simultaneous Reproduction of Quartz and Orthoclase.** By P. HAUTEFEUILLE (*Compt. rend.*, 90, 830—831).—Many phosphates bring about the crystallisation of silica in the form of tridymite. The phosphates of potassium and sodium also attack the aluminosilicates. Potassium aluminosilicate, at about  $1,000^\circ$ , crystallises in the form of orthoclase adularia. The simultaneous production of quartz and orthoclase cannot be accomplished by means of a pure phosphate, since the latter only acts on the silica at a very high temperature. By the addition of a fluorine compound, however, the temperature necessary to effect this is lowered, and crystals of quartz are obtained associated with those of felspar. The most highly developed faces of the quartz crystals are  $e^2$ ,  $p$ , and  $e^1$ , and these are very deeply striated. The orthoclase has a stony appearance, and the crystals are generally twinned like those found in trachytes. The author considers it probable that the crystals of orthoclase found on the bricks of metallurgical furnaces have been formed by the action of alkaline fluophosphates volatilised and carried away in the furnace gases. By heating a mixture of acid potassium phosphate (previously fused with silica and alumina) with silica and a small quantity of potassium fluosilicate in a glass tube, one part of which contained fragments of porcelain, he obtained crystals of orthoclase together with quartz, not only on the part of the tube containing the mixture, but also on the pieces of porcelain.

C. H. B.

**The Micas.** By G. TSCHERMAK (*Jahrb. f. Min.*, 1878, 950—952).—In a previous paper, the author considered the crystallographical and optical properties of the micas (*Jahrb. f. Min.*, 1878, 71). The present communication treats of the composition of the various combinations occurring in the different micas, and shows that most of the micas are complicated compounds, all containing the same nucleus or kernel, round which the other combinations are grouped. Tschermak arranges the micas in the following groups, viz. :—

**Biotite group** (*magnesia-mica partly*).—Monosymmetrical; typical forms  $\text{OP}$ , +  $\text{P}$ , —  $\frac{1}{2}\text{P}$ ,  $\infty\text{R}\infty$ . Optically negative, the first bisectrix " $a$ " differing very little from the normal on " $c$ ." The sp. gr. increases with the amount of iron, and varies from 2.8 to 3.2.

**Anomite.**—The plane of the optical axes is parallel to " $b$ ,"  $p > v$ .

Composition =  $\text{Si}_2\text{Al}_6\text{K}_3\text{H}_3\text{O}_{24}$  +  $\text{Si}_2\text{Mg}_{12}\text{O}_{24}$  in the proportions 1 : 1 or 2 : 1.

*Rubellan*, *voigtite*, *eukamptite*, *aspidolite*, *hallite*, *raetolite*, are more or less altered meroxene.

*Lepidomelane*.—The plane of the optical axes is parallel to "b." Chemical composition =  $\text{Si}_2\text{Al}_6\text{K}_3\text{H}_3\text{O}_{24}$  +  $\text{Si}_2\text{Al}_4\text{O}_{24}$ . Sometimes varying amounts of the iron-compound corresponding to the first-mentioned silicate occur vicariously. The pterolite of Breithaupt is probably lepidomelane.

*Phlogopite Group*.—Monosymmetrical typical forms =  $0\text{P.} + \text{P} - \frac{1}{2}\text{P.} \infty \text{R} \infty$ . Optically negative; "a" deviating  $2\frac{1}{2}$  from the normal to "c." The plane of the optical axes is parallel to "b." Sp. gr. varies from 2.75 to 2.97.

*Phlogopite*.—Composition =  $\text{Si}_2\text{Al}_6\text{K}_3\text{O}_{24}$  +  $\text{Si}_{10}\text{H}_3\text{O}_{24}$  and  $\text{Si}_2\text{Mg}_{12}\text{O}_{24}$ , these compounds often occurring in the proportions 3 : 1 : 4. Sometimes the isomorphous compound,  $\text{Si}_{10}\text{O}_3\text{Fl}_{24}$ , occurs in the place of the second compound,  $p < v$ . The reddish-brown phlogopites all contain fluorine, whilst the green ones contain very little, hence it is often difficult to distinguish between the latter and meroxene. One characteristic of the phlogopites is their occurrence in granular limestone. The vermiculite of Webb, and the jefferisite of Brush are most likely decomposed phlogopite.

*Zinnwaldite* (lithionite of von Kobell, rabenglimmer of Breithaupt, and kryophyllite of Cooke).—Chemical composition =  $\text{Si}_2\text{Al}_6\text{K}_3\text{O}_{24}$  +  $\text{Si}_2\text{Fe}_{12}\text{O}_{24}$  +  $\text{Si}_{10}\text{Fl}_{24}\text{O}_8$ , these compounds occurring in the proportions 10 : 2 : 3. The potassium compound is occasionally half replaced by the analogous lithium compound, and the fluorine compound by the corresponding hydrogen compound,  $p > v$ .

*Muscovite Group*.—Monosymmetrical; typical forms  $0\text{P.} - 2\text{P.} \infty \text{R} \infty$ . Optically negative, "a" deviating slightly from the normals. The plane of the optical axes perpendicular to "b,"  $p > v$ . Sp. gr. varies from 2.83 to 2.89.

*Lepidolite* (lithia-mica).—Chemical composition =  $3\text{Si}_2\text{Al}_6\text{K}_3\text{O}_{24}$  +  $\text{Si}_{10}\text{O}_3\text{Fl}_{24}$ , where the potassium compound is partially replaced by the corresponding lithium compound, and the fluorine compound partially replaced by the corresponding hydrogen compound. Probably the cookeite of Brush is a variety of this mineral.

*Muscovite* (potash-mica, diaxial-mica, phengite, fuchsite, chromium-mica).—Chemical composition =  $\text{Si}_2\text{Al}_6\text{K}_3\text{H}_3\text{O}_{24}$  +  $\text{Si}_{10}\text{H}_3\text{O}_{24}$ ; both of these compounds occurring in the proportions of 3 : 1 in phengite. Didymite and amphigolite are names for varieties of muscovite. Margarodite and euphyllite are mixtures of muscovite with the following micas, viz., *allacherite*, a muscovite containing barium; *sericite*, a muscovite containing magnesia-mica; *damourite*, a massive muscovite, sometimes called *onkosine*; *liebenerite* and *pinite* are composed mostly of muscovite.

*Paragonite* (pregratite, sodium-mica).—Chemical composition =  $\text{Si}_2\text{Al}_6\text{Na}_3\text{H}_3\text{O}_{24}$ .

*Cossairite* is massive paragonite.

*Margarite Group*. *Margarite* (perglimmer, corundellite, clingmanite, emerylite, diphanite).—Monosymmetrical; typical forms



$0P.\infty P\infty - \frac{1}{2}P. + \frac{1}{4}P.$  Optically negative, "a" deviating as much as  $6^\circ$  from the normals to "c,"  $p < v$ . Sp. gr. varies from 2.95 to 3.1. Chemical composition =  $Si_4Al_6Ca_2H_4O_{24}$ . A sodium silicate is intermixed with it in minute quantity. The *dudleyite* of Gentz is probably an altered margarite. Margarite is nearly related to the clintonite-group on account of its brittleness and optical properties, although its oxygen-ratio is that of a true mica. *Astrophyllite*, which is also nearly related to clintonite, is not a mica. C. A. B.

**Crystal-system of Cyanite.** By G. RATH (*Jahrb. f. Min.*, 1878, 952).—Owing to the absence hitherto of terminal faces, the relation between the vertical axis and the lateral axis could not be ascertained. The author obtained the missing information from the examination of a fine crystal from the Greiner in Tyrol, and a crystal from Monte Campione led to the discovery of a new twin-law. The axial ratio of the brachy-axis, macro-axis, vertical axis =  $0.9164 : 1 : 0.70996$ . The vertical and macro-axes intersect at an angle of  $90^\circ$ . Besides the already well-known forms, the following new ones were observed, viz.,  $P. . P. . 2P_2 . 2P . P_2 . 2P_2 . \infty P_2 . P_\infty . P_\infty . 2P_\infty . P_\infty . \frac{1}{2}P_\infty . \infty P_\infty : 0P = 101^\circ 16\frac{1}{2}'$ ,  $\infty P : 0P = 99^\circ 17'$  (calculated). The new twin-law observed on the Monte Campione crystal was "the twin-plane the basal terminal plane." C. A. B.

**Crystal Forms of Epidote.** By H. BÜCKING (*Jahrb. f. Min.*, 1878, 956—958).—The author adopts the orientation of Marignac, and takes also the axial ratios of von Kokscharow, viz.,  $a : b : c = 1.5807 : 1 : 1.8057$ .  $\beta = 64^\circ 36'$  as the basis of the various calculations.

*Epidote from the Sulzbachthal.*—The crystals from this locality attain sometimes a length of 120 mm., and are always developed in the direction of the ortho-axis, whilst the zone of the hemidomes is very prominent. The common forms observed are  $0P. \infty P_\infty . P_\infty .$  and  $P$ . The crystals are either single, or twinned parallel to the orthopinacoid. The author was enabled to add many new forms to the great number already known, the final result proving that epidote from this neighbourhood exhibits 172 distinct forms.

*Epidote from Arendal* is characterised by the great size and a peculiar shell-like or zonal structure of the crystals. The number of forms exhibited by epidote from this locality is 29. The crystals are generally rich in faces, sometimes single and sometimes twinned (twin-plane  $\infty P_\infty$ );  $0P$  predominates in the zone of the hemidomes, whilst  $\infty P_\infty$  is often very slightly developed; the commonest domes are  $P_\infty$  and  $2P_\infty$ , and with these  $P$  and  $\infty P$  occur.

*Epidote from Striegau.*—Crystals from this locality are curtailed in the direction of the ortho-axis. Twin formation is not observed, whilst the number of forms is 17.

*Epidote from the Fassathal and Allochethal.*—These crystals are occasionally complete at both ends, and attain sometimes a length of from 5 to 10 mm. The forms commonly observed are  $P_\infty . \frac{1}{2}P_\infty . 2P_\infty . 0P . \infty P_\infty$  and  $\infty P$ . No twins.

*Epidote from Guttannen in the Bernese Oberland.*—Two types of crystals are observed here, the first and commonest being characterised by

the prominence of the clinopinacoid; whereas in the second type it is entirely absent. The crystals of the first type are generally tabular, through the predominance of  $OP$  or  $\infty P\infty$ ;  $\infty P\infty$  is very prominent and strongly striated.  $P$  is also much developed, and the prisms  $\infty P$  and  $\infty P2$  occur often together.

*Epidote from Traversella* is characterised by the occurrence of a long vertical prismatic type, through the predominance of  $\infty P$ , the crystals sometimes attaining a length of 20 mm. There is also a second type, the crystals in this case being developed in the direction of the ortho-axis, with  $\infty P$  very much developed. The faces in the zone of the hemidomes are strongly striated. Twins common according to the usual laws. The epidote from Traversella exhibits 17 distinct forms.

*Epidote from Bourg d'Oisans*.—The crystals from this locality have long been known, and are characterised by a peculiar development parallel to the axis of symmetry (clino-axis); they are very strongly striated, grouped together almost parallel to each other, and in sheaves. The clinopinacoid is the predominating side form. The author gives the results of his examination of epidote from other localities, which are, however, of less interest than those above referred to. The result of Bucking's labour is the addition of 147 distinct forms to the 73 already known, making the total number of forms known to occur on epidote 220. He arranges all these in tables according to their zones, giving at the same time the interfacial angles with corrected angles for the previously known forms.

C. A. B.

**Lintonite and other Forms of Thomsonite.** By S. F. PECKHAM and C. W. HALL (*Amer. J. Sci.* [3], 19, 122).—These varieties of thomsonite occur in cavities in a dark-coloured rock related to diabase, at Grand Marais, Lake Superior; considerable quantities are also found on the beach beneath the rock, in the form of round, smoothly polished pebbles. Three principal varieties were distinguished.

(I.) Opaque, white, almost conchoidal in fracture, structure but very slightly fibrous.

(II.) Ordinary thomsonite, of various colours, but always hard and fibrous; and (III) opaque and chrome-green in colour, shading out in some to colourless, and translucent with a conchoidal or uneven fracture.

The hardness of all these varieties is generally between 5 and 6. Some fibres scratch quartz ( $H = 7$ ). The sp. gr. is 2.33—2.35. Fracture of I and II fibrous, of III very uneven, and in all directions with equal facility. With hydrochloric acid they form a thick jelly. Grains of metallic copper frequently occur in them, especially in No. III.

(I.) This form is, as already mentioned, opaque and porcelain-like in appearance, sometimes banded with transparent or with yellow bands; its composition is as under—

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $CaO$ | $K_2O$ | $Na_2O$ | $H_2O$         |
|---------|-----------|-----------|-------|--------|---------|----------------|
| 40.45   | 29.50     | 0.232     | 10.75 | 0.357  | 4.766   | 13.93 = 99.985 |

(II.) Specimens of this type are fibrous and radiated from one or more centres; the mineral sometimes fills seams and cavities, the

centres of radiation then being close together, and the mineral breaking easily at the points of juncture of the various systems of concretion. Transparent needles often occur penetrating the masses from the surface to about halfway towards the centre; these act strongly on polarised light.

The composition of this variety is—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaO.  | K <sub>2</sub> O. | Na <sub>2</sub> O. | H <sub>2</sub> O. |
|--------------------|----------------------------------|----------------------------------|-------|-------------------|--------------------|-------------------|
| 46.020             | 26.717                           | 0.813                            | 9.400 | 0.390             | 3.756              | 12.800 = 99.896   |

(III.) This variety was first supposed to be prehnite, but its composition and sp. gr. show that it is, at any rate closely allied to, thomsonite. Its sp. gr. is 2.32—2.37, and its composition as follows:—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | FeO. | CaO.   | K <sub>2</sub> O. | Na <sub>2</sub> O. | H <sub>2</sub> O. |
|--------------------|----------------------------------|------|--------|-------------------|--------------------|-------------------|
| 40.605             | 30.215                           | 0.40 | 10.370 | 0.49              | 4.055              | 13.75 = 99.885    |

In its structure, however, it differs greatly from thomsonite, being finely granular instead of fibrous. The iron also is combined as ferrous oxide, instead of being a mechanical admixture of ferric oxide.

The mineral, which the author proposes to call *lintonite*, occurs either in small rounded pebbles, or as a crust on the exterior of the previous minerals.

The silica in No. II is considerably higher than in I and III, but it is probable that, taking its exceptional hardness into account, it contains free silica. If the composition of II be calculated with 40.43 per cent. SiO<sub>2</sub>, and the iron in all three be omitted, their compositions come out practically identical. Compared with ordinary thomsonite, these minerals have a higher percentage of silica and of water, part of the latter being probably basic.

C. W. W.

**Some Points in Lithology. II. Composition of the Capillary Volcanic Glass of Kilanea, Hawaii, called Pélé's Hair.** By J. D. DANA (*Amer. J. Sci.* [3], 18, 134).—The composition of this substance closely resembles that of ordinary dolerite; the following figures show the relative composition of the two substances, the first line giving the mean of two analyses of Pélé's Hair, the second the results of an analysis by G. W. Hawes of the "trap" of West Rock, New Haven, Conn., U.S.:—

|         | SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | FeO.                            | MnO.  | MgO.    |
|---------|--------------------|----------------------------------|----------------------------------|---------------------------------|-------|---------|
| I ....  | 50.75              | 16.54                            | 2.10                             | 7.88                            | trace | 7.65    |
|         | CaO.               | Na <sub>2</sub> O.               | K <sub>2</sub> O.                | P <sub>2</sub> O <sub>5</sub> . | Ign.  |         |
|         | 11.96              | 2.13                             | 0.56                             | —                               | 0.35  | = 99.92 |
|         | SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | FeO.                            | MnO.  | MgO.    |
| II .... | 51.80              | 14.21                            | 3.55                             | 8.26                            | 0.42  | 7.63    |
|         | CaO.               | Na <sub>2</sub> O.               | K <sub>2</sub> O.                | P <sub>2</sub> O <sub>5</sub> . | Ign.  |         |
|         | 10.68              | 2.15                             | 0.39                             | 0.14                            | 0.63  | = 99.72 |

The "trap" consists essentially of labradorite and augite, with some magnetite.

The following details respecting the microscopic characters of Pélé's Hair are given by C. F. W. Kruckenberg:—The fibres are sometimes bent and coalesce into loops; they are often tubular, frequently contain air-bubbles, and occasionally microlites. The fibre is usually enlarged where a crystal (or microlite) or an air-bubble occurs. The crystals are mostly rhombic.

C. W. W.

**The Eruptive Rocks in the Saar and Moselle Districts.** By A. v. LASAULX (*Jahrb. f. Min.*, 1878, 955—956).—The eruptive rocks of the devonian formation between the Moselle and the Saar, consist (in the northern portion of the neighbourhood of the Moselle) of diorite and diabase. These rocks are also common to the west of the Saar as far as the Ardennes. Further south, near the younger "Zeshstein" and "rothliegenden" formations, melaphyr and porphyry occur. The diorites are characterised throughout by light green and mostly fibrous hornblende, whilst augite is generally absent. The diabase contains light-grey or reddish augite, which has occasionally a diallagite-like cleavage; hornblende is also observed in it sometimes. Between the two rocks mentioned stands the rock of Kürenz, which is a diorite-diabase containing the augite of the diabase, the hornblende of the diorite, and in addition dark-green hornblende, some biotite, and as a characteristic, urallite. The secondary products of the decomposition of the diabases are viridite, calcite, and very little epidote. The viridite is a chloritic mineral in both rocks, and has not a constant composition; it sometimes resembles dilessite and sometimes helminth.

Titanic-iron, magnetite, and iron-pyrites are present in both rocks, the latter predominating in the diabase, whilst the titanio-iron is present in greater quantity than the magnetite. The melaphyrs are characterised by a preponderance of "base," but its amount varies. Some melaphyrs are poor in olivine. Three stages of decomposition are observed on these melaphyrs, viz.: (1.) Where the augite and plagioclase is clear, the "base" partially unchanged and partially altered into viridite, the olivine mostly fresh, but the granules are penetrated with veins of viridite, lastly the magnetite is still fresh, but surrounded with a brown zone. Calcite is rare. (2.) The plagioclase appears clouded in zones, the augite and "base" is changed into viridite, the olivine is completely converted into viridite, and contains freshly formed magnetite, "brown-iron" in and about the olivine, but only sparingly in the "ground-mass," primary magnetite completely changed into oxide of iron, and lastly, calcite in large amount. (3.) The plagioclase appears completely clouded, the characteristic striation being scarcely apparent, whilst the outlines only of the plagioclase are defined by oxide of iron, all the viridite has disappeared, and is changed into oxide of iron, which now imparts its colour to the whole rock, the olivine is also converted into oxide of iron, there is no newly-formed magnetite, almost all the calcite has been washed away, whilst silicic acid has more or less replaced it. The final products of the various processes of decomposition are:—

(1.) From the *diorites*, limestone rich in epidote (epidosite). (2.) From the *diabase*, limestones containing serpentine and dolomite (ophicalcite). (3.) From the *melaphyrs*, aluminous and quartzose brown-ironstone.  
C. A. B.

## Organic Chemistry.

**Action of Potassium Carbonate on Isobutaldehyde.** By F. URECH (*Ber.*, 13, 483—484).—The author attempts to determine the rate of polymerisation of isobutaldehyde by measuring the contraction which a given volume of isobutaldehyde undergoes when left in contact with potassium carbonate for intervals of time varying from 5 minutes to 10 hours.  
W. C. W.

**Diiodopropyl Alcohol and Moniodoallyl Alcohol.** By H. HÜBNER and E. LELLMANN (*Ber.*, 13, 460—461).—*Duodopropyl alcohol*,  $C_3H_5I.OH$ , is prepared by adding a solution of iodine in chloroform to allyl alcohol diluted with three times its volume of chloroform. The compound crystallises in colourless needles, which are insoluble in water, but dissolve in alcohol. The crystals decompose under the influence of light or heat.

*Moniodoallyl alcohol*,  $C_3H_4I.OH$ , prepared by warming the solution of the preceding compound in chloroform, or by treating the solution with dilute sodium carbonate, forms needle-shaped crystals (m. p.  $160^\circ$ ). A third body appears to be formed by the action of a concentrated solution of potash on diiodopropyl alcohol.  
W. C. W.

**Ulmic Compounds formed from Sugar by the Action of Acids.** By F. SESINI (*Gazzetta*, 10, 121—136).—The author discusses the results hitherto obtained in this reaction, and as they are far from concordant, resolved to reinvestigate the subject. He finds that the formula attributed to the product by Mulder is incorrect, for this chemist dried the substance at  $140$ — $165^\circ$ , whilst it is decomposed a little above  $100^\circ$ , giving off volatile carbon compounds, and amongst others, formic acid. Moreover, the crude product of the action of acids on cane-sugar consists of at least two substances, one of which, *saculmic acid*, is soluble, whilst the other, *saculmin*, is insoluble in cold alkaline solutions.

Following Malaguti's process, a brown voluminous product was obtained, amounting, however, to only about 3 per cent. of the cane-sugar employed. A microscopic examination showed that it consisted of numerous minute spheres or vesicles, and not of scales or plates, as might be supposed from the appearance to the naked eye. This product is formed abundantly during the first 12 hours' boiling of the acidulated sugar solution, but the quantity produced then gradually decreases, and ceases almost entirely after 40 hours with acid 1 : 30. This is due to the conversion of the sugar into other products, and not

to exhaustion of the acid. The quantity of sugar transformed into this product is relatively small, it being very difficult to obtain as much as 10 per cent. from the sugar. In the course of this action, the principal product during the first period is saculmin, then saculmin and saculmic acid are formed in nearly equal portions, and at last much more saculmic acid is produced than saculmin. The author has made experiments which show that the saculmin is formed from the cane-sugar, whilst the saculmic acid is a product of the decomposition of the glucose arising from the inversion of the cane-sugar: pure glucose gave a product which was completely soluble in potash solution.

During the ulmification of sugar, an appreciable quantity of volatile acids is produced, besides some carbonic anhydride: the acids are formic acid, a little acetic acid, and perhaps acids higher in the series; at the same time there appears to be present a substance which becomes converted into formic acid in contact with the air, possibly formic aldehyde. The carbonic anhydride observed is in all probability due to decomposition of the formic acid.

From these results it would seem most probable that the ulmic matters instead of being formed from the carbohydrates by simple dehydration, are really formed from saccharine substances by the simultaneous elimination of the elements of water, and of volatile carbon compounds.

C. E. G.

**Compound of Levulose with Lime.** By E. PELIGOT (*Compt. rend.*, 90, 153—156).—In order to obtain the lime-compound of levulose in a state of purity, a 6 or 8 per cent. solution of inverted sugar is mixed with milk of lime, the liquor quickly filtered and cooled to 0°, when the so-called calcium levulosate crystallises out in abundance. The crystals must be washed quickly to prevent absorption of carbonic anhydride, and dried in a vacuum. 100 parts of water at 15° dissolve 0.73 part of the salt, producing a solution which is exceedingly prone to alteration, its alkaline reaction becoming gradually weaker, and its amber-yellow colour passing to deep brown. When boiled, the solution quickly becomes neutral, and a precipitate is obtained similar to that which appears always to accompany the formation of glucic acid.

The analysis of the pure yellowish-white lime compound, dried in a vacuum, leads to the formula  $C_6H_{12}O_6 \cdot CaO \cdot H_2O$ , containing 22.0 per cent. of lime: when dried in presence of quicklime only, a dihydrate is obtained, which, unlike the stable monohydrate above mentioned, cannot be preserved even in well-closed bottles; it is slowly transformed into a brown viscous substance, which appears to contain both glucic and saccharic acids. By means of calcium levulosate and oxalic acid, a solution of pure levulose can be prepared, but all attempts to induce this solution to crystallise have hitherto proved unsuccessful.

J. W.

**Rate of Substitution by Bromine in the Acetic Acid Series.** By C. HELL (*Ber.*, 13, 531—541).—Small tubes containing weighed quantities of bromine and the acid were heated at 100° for a given time, the tubes were then opened in a solution of potassium iodide,

and the amount of iodine liberated by the free bromine was determined by titration with a solution of sodium thiosulphate. From these experimental data the rate of substitution can easily be calculated. The process is divided into three stages, 1st, a period of feeble action, which lasts until 10—20 per cent. of the bromine present has entered into the reaction; 2nd, a period of rapid substitution, during which from 10 to 60 per cent. of the bromine combines. In the final stage the rate of substitution diminishes.

The duration of the first stage of substitution diminishes as the molecular weight of the acid increases. In the case of isobutyric and valerianic acids, the number of molecules which have taken part in the reaction is proportional to the time. The rate of substitution increases with the temperature.

The author believes that when bromine is brought into contact with a fatty acid, the two bodies exist together in a comparatively inert state until a certain amount of hydrobromic acid has been liberated, which promotes the formation of an addition compound. Substitution now takes place rapidly, since the fatty acid and the bromine are now in close juxtaposition.

The preparation of substitution products is greatly facilitated by saturating the fatty acid with hydrobromic acid gas before submitting it to the action of bromine. W. C. W.

**The Acids which are formed by the Distillation of the Crude Fatty Acids in a Current of Superheated Steam.** By A. CAHOURS and E. DEMARÇAY (*Compt. rend.*, 90, 156—158).—By redistillation in a current of superheated steam, the crude fatty acids resulting from the saponification of the neutral fats, are partly resolved into a number of simpler acids of the acetic series. Thus, butyric, valeric, caproic, cenanthylic, and caprylic acids are formed, all apparently belonging to the normal series. The predominating acids in the first sample were caproic and cenanthylic, whilst butyric, and perhaps pelargonic, were present in small quantity only.

Another specimen of 135 grams resulting from the distillation of nearly 200,000 kilos. of crude acids, gave as principal product a liquid boiling between 162° and 164°, which had the composition and properties of normal butyric acid; the last portions which distilled between 180° and 190° were chiefly valeric acid. From the more volatile portions of the distillate, two liquids were obtained boiling between 106—122° and 135—145°, these after a most careful investigation were proved to be acetic and propionic acids respectively.

A third sample of 180 grams boiling between 102° and 168° was etherified by distilling it with methyl alcohol and sulphuric acid. On fractionating the product, ethers were obtained boiling at 35°, 55°—58°, and 76°—80°, which on saponification were found to contain respectively formic, acetic, and propionic acids.

The authors therefore have proved that in the distillation of the more complex fatty acids in a current of superheated steam, a partial resolution into simpler terms of the acetic series takes place, they have isolated and prepared in a state of purity all the acids from formic to caprylic; while they do not doubt the presence of higher members of

the series such as pelargonic and capric, they have not been able on account of their small proportion and high boiling point to effect their satisfactory separation.

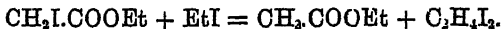
Independently of the acids of the fatty series, a small quantity of acids belonging to the succinic series appears to be produced; sebacic acid was certainly recognised, but the other acid or acids could not be purified sufficiently to admit of their recognition. They appeared to be lower homologues of sebacic acid. J. W.

**Preparation of Ethyl Acetate.** By J. A. PARST (*Bull. Soc. Chim.* [2], 33, 350—351).—A cooled mixture of 50 c.c. sulphuric acid and 50 c.c. alcohol is placed in a flask and heated at  $140^{\circ}$ , a mixture of equivalent parts of alcohol and acetic acid, being allowed to run in slowly; at first a little ether distils over, but after a short time ethyl acetate is given off. The reaction commences at  $130$ — $135^{\circ}$ , whilst at  $145^{\circ}$  sulphurous anhydride is evolved.

The distillate is washed with a saturated solution of calcium chloride, and dried over fused calcium chloride. Pure ethyl acetate is insoluble in a solution of calcium chloride, but if it contains 30 per cent. alcohol, calcium chloride solution dissolves appreciable quantities. A mixture of 1 vol. ethyl acetate, and 1 vol. alcohol, forms a homogeneous mixture with 2 vols. of a solution of calcium chloride. By the above method 90 per cent. of the theoretical yield of ethyl acetate may be obtained. The reaction which takes place is similar to that in the formation of ether by the action of sulphuric acid on alcohol.

Methyl acetate may be prepared in a similar manner. When a mixture of alcohols is used, a mixture of acetates is produced, corresponding with the alcohols taken. L. T. O'S.

**Action of Ethyl Iodide on Ethyl Iodoacetate.** By L. ARONSTEIN and J. M. A. KRAMPS (*Ber.*, 13, 489—491).—When a mixture of ethyl iodide and ethyl iodoacetate is heated in sealed tubes at  $130^{\circ}$ , ethyl acetate, ethane, and ethylene iodide (m. p.  $82^{\circ}$ ) are produced—



Ethylene iodide is also formed in small quantity when either ethyl iodide or ethyl iodoacetate is heated at  $130^{\circ}$ . W. C. W.

**Some Derivatives of  $\beta$ -Chlorobutyric Acid.** By L. BALBIANO (*Gazzetta*, 10, 137—148).—When alcoholic ammonia in large excess acts on ethyl  $\beta$ -chlorobutyrate, taking care that the temperature does not rise above  $70^{\circ}$ , it yields ammonium chloride and  $\beta$ -amidobutyramide thus:  $\text{CHMeCl.CH}_2\text{COOEt} + 3\text{NH}_3 = \text{CHMe}(\text{NH}_2).\text{CH}_2\text{CONH}_2$ . The amide may be separated as platinochloride in distinct yellowish-red crystals, sparingly soluble in alcohol, and insoluble in ether. On decomposing the platinochloride with the theoretical quantity of potash a syrupy substance is obtained which is probably the amide, but it does not crystallise. It is decomposed when boiled with lead hydrate, ammonia being evolved, and after removing the lead by hydrogen sulphide and evaporating, a deliquescent mass of crystals of  $\beta$ -amidobutyric acid,  $\text{CHMe}(\text{NH}_2).\text{CH}_2\text{COOH}$ , is obtained. The hydrochloride



of  $\beta$ -amidobutyramide obtained by decomposing the platinochloride with the theoretical amount of ammonium chloride is a crystalline deliquescent mass. The yield of the amide obtained in the above reaction is but small, by far the larger portion of the  $\beta$ -chlorobutyric acid being converted into resinous products.

In a similar manner, when aniline acts on  $\beta$ -chlorobutyric acid the *anilide of  $\beta$ -anilobutyric acid* is formed, and may be obtained in the form of the hydrochloride,  $\text{CHMe}(\text{NPh} \cdot \text{HCl}) \cdot \text{CH}_2 \cdot \text{CONPhH}$ . This substance, which is with difficulty purified from the resinous matter which accompanies it, crystallises in small lustrous plates, only moderately soluble in cold alcohol, but very readily when it is hot, very sparingly soluble in hot water, and insoluble in ether; it melts at  $207^\circ$ .

A small quantity of another crystalline substance of the formula  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}$  is also produced in the reaction between aniline and dichlorobutyric acid. It is only sparingly soluble in cold water, moderately in water or alcohol when hot. It crystallises in large nodules (m. p.  $137-139^\circ$ ). This substance, on examination, was found to be the oxalate of a base,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ , which undergoes decomposition when boiled with baryta, forming the barium salt of *anilobutyric acid*,  $\text{CMeH}(\text{NPhH}) \cdot \text{CH}_2 \cdot \text{COOH}$ . The author regards this base as analogous to a betaine of the butyric series in which only one of the nitrogen valencies is saturated by a negative radicle, and proposes for it the formula  $\text{O} < \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{NPhH}_2 \end{smallmatrix} > \text{CHMe}$ , that of  *$\beta$ -butylhydrophenylbetaine*.

The base forms a hygroscopic crystalline mass, very soluble in alcohol and ether. The platinochloride is obtained as a crystalline precipitate by adding ether to its alcoholic solution.  $\beta$ -anilobutyric acid crystallises from its aqueous solution in tufts of needles (m. p.  $128^\circ$ ), sparingly soluble in cold water, more so in alcohol or ether. The *barium salt*,  $(\text{C}_{10}\text{H}_{13}\text{O}_2\text{N})_2\text{Ba}$ , crystallises in scales which are only very sparingly soluble in cold water and almost insoluble in alcohol even when boiling. The mechanism of the reaction in which these compounds is produced is far from simple, as is shown by the amount of resinous products formed.

C. E. G.

**Action of Finely Divided Silver on Ethyl Monobromobutyrate.** By C. HELL and O. MÜLHAUSER (*Ber.*, 13, 473-479).—A complicated reaction occurs when ethyl monobromobutyrate is subjected to the action of finely divided silver; ethyl bromide, ethyl alcohol, ethyl butyrate, and a mixture of isomeric ethyl suberates (b. p.  $245-247^\circ$ ) are formed.

In order to isolate the isomeric acids, the portion of the crude product, boiling between  $238^\circ$  and  $290^\circ$ , is treated with strong hydrobromic acid at  $100^\circ$ , when a crystalline deposit separates out on cooling. The contents of the tube are neutralised with soda and boiled to remove the undecomposed ethereal salts, the liquid is then acidified with dilute sulphuric acid and distilled in a current of steam, when an oily, uncrystallisable acid passes over. Ether extracts two acids from the residue, which can be separated by recrystallisation from hot water. The more soluble acid melts between  $110-125^\circ$ , the less soluble acid melts between  $170-180^\circ$ .

A hydroxysuberic acid,  $C_8H_{14}O_6$ , is formed as a secondary product if the hydrobromic acid contains free bromine. W. C. W.

**Acids of the Formula  $C_8H_{14}O_4$ , derived from Bromobutyric Acid.** By C. HELL and O. MÜLHAUSER (*Ber.*, 13, 479—482).—The formation of three acids by the action of hydrobromic acid on the mixture of ethereal salts, which is produced by treating ethyl bromobutyrate with finely divided silver, has been described in the preceding abstract.

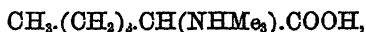
The volatile acid is a clear oil which is soluble in alcohol, ether, and also to some extent in water. It has almost the same sp. gr. as water. The silver salt has the composition  $C_8H_{12}O_4Ag_3$ . The small quantity of the substance obtained did not permit of its identity with isocrotonic acid being clearly established, although it closely resembles the latter in certain points.

The two crystalline acids can be easily separated by recrystallisation from 20 parts of hot water, or by adding dilute sulphuric acid to a solution of the sodium salts, when the less soluble acid is precipitated and the acid of low melting point remains in solution.

The sparingly soluble acid crystallises in white, microscopic needles, m. p. 184—185°; at a higher temperature a portion of the acid sublimes, but the rest decomposes, forming an oily anhydride soluble in alcohol, ether, and hot water. The ethyl salt of this acid is not attacked by alkalis at 100°, although it is saponified by hydrobromic acid at this temperature.

On heating the acid, m. p. 127°, it changes into a liquid anhydride. The ethyl salt of this acid is slowly saponified by alkalis at 100°. The discovery of these two crystalline acids increases the number of isomeric suberic acids to five. W. C. W.

**Amido-acids from  $\alpha$ -Bromocaproic Acid.** By E. DUVILLIER (*Compt. rend.*, 90, 822—824).—*Methyl-amido- $\alpha$ -caproic acid*,



is obtained by heating  $\alpha$ -bromocaproic acid with an aqueous solution of methylamine in a closed tube at 100° for several hours. It is a white crystalline substance soluble in 9.8 parts of water at 11°, and much more soluble in boiling water; slightly soluble in cold, but readily soluble in hot alcohol, from which it is deposited in nacreous plates, insoluble in ether. The acid may be heated to 110° without change, but at a higher temperature it volatilises without fusing, and gives off ammonia. It gives no reaction with mercurous or silver nitrate, but with ferric chloride an intense red coloration is produced, and on boiling a yellowish-brown precipitate is thrown down. The hydrochloride crystallises in anhydrous transparent flakes, very soluble in water and alcohol, but insoluble in ether. The platinochloride forms orange crystals extremely soluble in water, very soluble in alcohol, but only sparingly soluble in ether. With cupric oxide this acid forms a beautiful pale-blue salt, containing  $2H_2O$ , which it loses at 110°.

*Ethyl-amido- $\alpha$ -caproic acid*, is obtained in the same way as the pre-

ceding compound, and has almost identical properties. It is, however, but little more soluble in hot than in cold water; the hydrochloride crystallises with difficulty, and the copper compound contains no water of crystallisation. The aqueous solutions of both acids have a neutral reaction and a bitter taste. C. H. B.

**Crystallised Oxalic Acid.** By A. VILLIERS (*Compt. rend.*, 90, 821—822).—Crystallised anhydrous oxalic acid,  $C_2H_2O_4$ , may be obtained by dissolving 1 part of the ordinary acid in about 12 parts of warm concentrated sulphuric acid, and allowing the solution to stand for several days. The anhydrous acid is deposited in remarkably transparent voluminous crystals of the form of octohedra with a rhombic base, generally modified by the face  $p$  of the primary prism, with a cleavage parallel to this face. When exposed to the air, the crystals take up two molecules of water and fall to powder.

C. H. B.

**Reducing Properties of Potassium-ferrous Oxalate.** By J. M. EDER (*Ber.*, 13, 500—502).—A solution of potassium ferrous oxalate is easily prepared by adding a concentrated solution of potassium oxalate to ferrous sulphate until the precipitate which is first produced redissolves, forming a dark-red liquid. It is a powerful reducing agent, not only in neutral but also in acid solutions. Platinum chloride, potassium platinochloride, and silver nitrate are rapidly reduced, and the chloride, bromide, and iodide of silver are slowly reduced to the metallic state by potassium ferrous oxalate. This reagent also reduces warm solutions of copper and mercuric salts, and rapidly decolorises Prussian blue and converts indigo blue to indigo white.

W. C. W.

**Oxypropionic Acid (Oxacrylic Acid).** By E. ERLENMEYER (*Ber.*, 13, 457—460).— $\beta$ -Chlorolactic acid,  $CH_2Cl.CH(OH).COOH$ , obtained by the action of nitric acid on monochlorhydrin, is identical with Richter's acid from epichlorhydrin (*J. pr. Chem.*, 20, 193), but is quite distinct from Melikoff's acid (*Ber.*, 12, 2227) prepared by treating acrylic acid with hypochlorous acid. Both acids yield the

same oxypropionic acid,  $\begin{array}{c} H_2C \\ | \\ O \end{array} \diagup CH.COOH$ , when acted on by alcoholic potash or soda.

On boiling the solution of the sodium or potassium salt, it is converted into glycerate. On distillation with dilute sulphuric acid, the acid is also changed into glyceric acid and a trace of aldehyde is formed, while sodium phenyloxypropionate under similar treatment yields phenyl-ethaldehyde.

The ready conversion of oxypropionic acid into  $\beta$ -chlorolactic acid, and of epichlorhydrin into unsymmetrical dichlorhydrin, seems to indicate that the epicyanhydrin of Pазschke (*J. pr. Chem.* [2], 1, 82) and Hartenstein (*ibid.* [2], 7, 297) is a polymeride, since it has not the property of combining directly with hydrochloric acid.

A crystalline compound, soluble in 72 parts of cold water, is formed, together with ammonium chloride, by heating  $\beta$ -chlorolactic acid with ammonia.

W. C. W.

**Reaction of Acetone with Potassium Cyanide, Thiocyanate, and Aqueous Hydrochloric Acid.** By F. URECH (*Ber.*, 13, 485—486).—The name *acetonylsulphocarbaminat*e is given to the compound  $C_2H_7NO_2S$ , which is formed by the action of potassium thiocyanate, cyanide, and aqueous hydrochloric acid on acetone (*Ber.*, 11, 467, this Journal, 1873, Abst., 488). The sulphur in this substance can be replaced by oxygen by means of lead oxide forming acetonyl carbamate (m. p.  $76^\circ$ ). Its melting point falls to  $67^\circ$ , if it is heated at  $120^\circ$  in a sealed tube for some hours. Both strong hydrochloric acid and baryta-water split up the compound into carbonic anhydride, acetic acid and ammonia.

Acetonylcarbamic acid is not decomposed by freshly precipitated oxide of silver, but combines with the metal forming  $C_2H_5AgNO_3$ . When nitrate of silver is added to the solution of a carbamate, a crystalline double salt having the composition  $(C_2H_7NO_2)_2AgNO_3$ , separates out.  
W. C. W.

**Formation of Tetramethylammonium Nitrate.** By E. DUVILLIER and A. BUISINE (*Compt. rend.*, 90, 872—874).—According to Juncadella (*Compt. rend.*, 1859), methylamine may be obtained by the action of methyl nitrate on an alcoholic solution of ammonia. The authors have substituted wood spirit for ethyl alcohol to avoid the formation of ethylamine. They find that when 1 mol. of methyl nitrate is heated in a closed tube at  $100^\circ$  with 1 mol. of ammonia, monomethylamine is the main product, but small quantities of the di- and triamines are also produced, together with a small quantity of tetramethylammonium nitrate.

When 1 mol. of methyl nitrate acts on 1 mol. of monomethylamine, about half the latter remains unchanged; small quantities of the di- and tri-methylamines are found, but the principal product is the tetramethylammonium nitrate. This substance is produced in still larger quantities when dimethylamine is heated with methyl nitrate. The liquid is heated with potash to expel volatile bases, neutralised with sulphuric acid, and the potassium salts are removed by concentration and repeated treatment with absolute alcohol. The tetramethylammonium nitrate is obtained in fine, anhydrous, lamellar crystals, which may be dried at  $130^\circ$  without undergoing alteration. It is not deliquescent, is very soluble in water, slightly soluble in cold, but more soluble in hot alcohol. It burns without leaving any residue, and is not decomposed by boiling with potash. When an aqueous solution of the substance is treated with hydrochloric acid and platinic chloride the platinochloride is deposited in the form of large orange-red regular octohedrons.  
C. H. B.

**Amines containing Tertiary Radicles.** By W. RUDNEFF (*Bull. Soc. Chim.* [2], 33, 297—300).—*Trimethylcarbamine*,  $CM_3NH_2$ , (b. p.  $45^\circ$ ), is obtained as a secondary product in the preparation of trimethylacetic acid from tertiary butyl nitrile. It is a mobile colourless liquid, having the characteristic odour of the amines. Its sp. gr. at  $0^\circ$  is 0.7137; 0.7054 at  $8^\circ$ ; and 0.6931 at  $15^\circ$ , giving the coefficient of dilatation 0.00217 between  $0^\circ$  and  $15^\circ$ . Its salts with hydrochloric,

nitric, and hydriodic acids are soluble in alcohol, ether, and water, and are not decomposed on boiling their aqueous solutions. The sulphate and oxalate are partially decomposed by cold water. By treating sulphuric acid with excess of the amine a mixture of neutral and acid sulphate is obtained. Trimethylcarbinamine readily unites with carbon bisulphide, forming a mixture of a salt of a thiocarbamine,  $\text{CS}(\text{NH}_2\text{C}_4\text{H}_9)(\text{S}\cdot\text{NH}_2\text{C}_4\text{H}_9)$ , and dibutylthiocarbamide,



The thiocarbamide cannot be obtained free from the urea.

*Dimethylethylcarbamine*,  $\text{CHMe}_2\text{Et}\cdot\text{NH}_2$  (b. p.  $78^\circ$ ); its sp. gr. is 0.7611 at  $0^\circ$  and 0.7475 at  $15^\circ$ . It is obtained as a bye-product in the preparation of dimethylethylacetic acid, and also by the action of mercuric cyanate on isoamyl iodide in presence of hydrochloric acid, which the author prefers to potash. Carbonic anhydride is evolved and isoamyl carbamide,  $\text{CO}(\text{NH}_2\text{C}_5\text{H}_{11})_2$ , is formed, which is heated at  $140^\circ$  with hydrochloric acid under pressure. The amine is a liquid dissolving in water with evolution of heat. Its properties and salts correspond with those of the isoamylamine of Wurtz.

*Dibutylamine*,  $(\text{C}_4\text{H}_9)_2\text{NH}$ .—By allowing a mixture of trimethylcarbamine and isobutyl iodide to stand for some time at the ordinary temperature crystals of dibutylamine hydriodide separate out. The reaction is not accelerated by heat, since the composition takes place with evolution of butylene. Dibutylamine yields trimethylcarbamine when treated with potash.

*Butylamylamine*.—Crystals of the iodide are obtained by allowing equal molecules of trimethylcarbamine and amyl iodide to stand at the ordinary temperature for about a week. The iodide decomposes spontaneously. Caustic soda and water decompose the amine with formation of amylene and trimethylcarbamine. L. T. O'S.

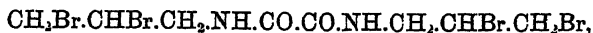
**Oxaethyline and Chloroxalallyline.** By O. WALLACH and G. STRICKER (*Ber.*, 13, 511—514).—The chlorine-atom in chloroxalallyline resists the action of nascent hydrogen, metallic magnesium, or aluminium, but it can be replaced by treating an alcoholic solution of the compound with sodium, or better by the action of phosphonium iodide on chloroxaethyline hydriodide,  $\text{C}_8\text{H}_{10}\text{ClN}_2\cdot\text{HI} + \text{H}_2\text{O}$ . This substance crystallises in beautiful transparent prisms, which melt in their water of crystallisation when heated on a water-bath. The anhydrous salt is hygroscopic.

*Oxaethyline*,  $\text{C}_8\text{H}_{10}\text{N}_2$ , is produced by heating this compound in sealed tubes with phosphorus and hydriodic acid. The crude product is rendered alkaline by the addition of potash, and the free base extracted with chloroform. Oxaethyline is a thick oily liquid miscible with water. It boils at  $213^\circ$ , and has the sp. gr. 0.9820. The aqueous solution produces precipitates with metallic salts. The hydrochloride,  $\text{C}_8\text{H}_{10}\text{N}_2\cdot\text{HCl}$ , is deliquescent; it forms a beautiful double salt with cadmium chloride. The platinochloride,  $(\text{C}_8\text{H}_{10}\text{N}_2\cdot\text{HCl})_2\text{PtCl}_4$ , forms reddish-yellow crystals, soluble in hot water. The crystalline silver salt,  $(\text{C}_8\text{H}_{10}\text{N}_2)_2\text{AgNO}_3$ , is soluble in alcohol and in hot water.

Two modifications of chloroxaethyline appear to exist, the ordinary

variety, which is freely soluble in light petroleum, and an isomeride insoluble in that solvent.

A solution of diallyloxamide (m. p. 154°, b. p. 274°) in chloroform combines with bromine to form the tetrabromide,



a white compound insoluble in chloroform and the usual solvents. It can, however, be recrystallised from glacial acetic acid. It decomposes at 220°.

*Chlororallyline* is formed by the action of phosphorus pentachloride on diallyloxamide, but it has not yet been obtained in a state of purity. W. C. W.

**Bases of the Oxalic Acid Series.** By O. WALLACH and E. SCHULZE (*Ber.*, 13, 514—516).—Chloroxaethyline is decomposed by sulphuric acid at 220° with evolution of hydrochloric acid. The mixture does not blacken. On oxidation with potassium permanganate, monethyloxamide and an acid melting at 111° are formed. The soluble compound with zinc chloride,  $(\text{C}_6\text{H}_9\text{ClN}_2.\text{HCl})_2.\text{ZnCl}_2$ , yields pyrrol and ammonia when distilled with potash.

Oxaethyline and methyl iodide combine with explosive violence, but if the substances are diluted with alcohol or ether the addition product,  $\text{C}_6\text{H}_{10}\text{N}_2.\text{MeI}$ , is obtained in white hygroscopic crystals, soluble in alcohol. The polyiodide crystallises in dark-green lustrous needles. Oxaethyline combines with bromine to form an oily compound, which yields an insoluble brominated base when treated with alkalis.

*Chloroxalpropyline*,  $\text{C}_6\text{H}_{13}\text{ClN}_2$  (b. p. 235°), is sparingly soluble in water. Both the platinumchloride and the silver salt are crystalline. *Chloroxalamyline*,  $\text{C}_{12}\text{H}_{21}\text{ClN}_2$  (b. p. 265—270°), is insoluble in water, but is volatile in a current of steam. W. C. W.

**Formation of Bases from Acid Amides.** By O. WALLACH and J. KAMENSKI (*Ber.*, 13, 516—525).—*Acetethylamide*,  $\text{MeCO}.\text{NH}.\text{Et}$ , on treatment with phosphorus pentachloride, forms the base  $\text{C}_6\text{H}_{13}\text{ClN}_2$ , which splits up when liberated from its salts, yielding the amidine,  $\text{C}_6\text{H}_{14}\text{N}_2$ , and acetic acid.

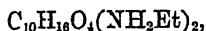
*Trichloracetethylamide*,  $\text{CCl}_3.\text{CO}.\text{NH}.\text{Et}$ , prepared from ethylamine and ethyl trichloracetate, crystallises in large colourless plates (m. p. 74°), which boil at 229—230°. With phosphorus pentachloride it yields an imide chloride,  $\text{CCl}_3.\text{CCl}:\text{NEt}$ , but no base. The dichloracetethylamide,  $\text{CCl}_2\text{H}.\text{CO}.\text{NH}.\text{Et}$  (m. p. 57°, b. p. 227°), yields with phosphorus pentachloride the imidechloride,  $\text{CCl}_2\text{H}.\text{CCl}:\text{NEt}$  (b. p. 161—164°), and the compound  $\text{CCl}_2\text{H}.\text{CCl}_2.\text{NEtPOCl}_2$ , which boils between 140° and 150°.

It has been previously shown (*Annalen*, 184, 196) that acetanilide under similar treatment gives the base  $\text{C}_{10}\text{H}_{13}\text{ClN}_2$ .

*Trichloracetanilide*,  $\text{CCl}_3.\text{CO}.\text{NHPh}$ , when treated with phosphorus pentachloride does not yield a base; but *monochloracetanilide*,  $\text{CClH}_2.\text{CO}.\text{NHPh}$ , forms a crystalline hydrochloride, which is deposited from hot alcohol in yellow needles.

*Acetmethylanilide*,  $\text{MeCO.NMePh}$ , also produces a hydrochloride under like conditions.

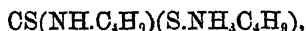
Phosphorus pentachloride acts on ethylamine camphorate,



forming a pale yellow liquid, which yields on distillation phosphorus oxychloride and a resinous mass containing a base, having the composition  $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}$  or  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}$ . The base is an oily liquid (sp. gr. 1.01 at  $20^\circ$ , b. p.  $284-286^\circ$ ) insoluble in water. It forms crystalline addition-compounds with silver nitrate, with methyl iodide and with bromine. The hydrochloride crystallises in prisms or plates, which are soluble in alcohol, and it forms a platinochloride. W. C. W.

**Remarks on the Preceding Papers.** By O. WALLACH (*Ber.*, 31, 522—524).—The author points out the relation between the bases of the oxalic series and some of the alkaloids, e.g., pyridine and piperidine. W. C. W.

**Thiocarbamides with Tertiary Radicles.** By W. RUDNEFF (*Bull. Soc. Chim.* [2], 33, 300).—*Tertiary butylthiocarbamide*,  $\text{Me}_3\text{C.NCS}$  (m. p.  $10.5^\circ$ , b. p.  $104^\circ$ ), is obtained by the action of mercuric chloride on the compound  $\text{CS}(\text{NH.C}_4\text{H}_9)(\text{S.NH}_3.\text{C}_4\text{H}_9)$  this vol., p. 546). It crystallises in large plates, having an aromatic odour. When treated with ammonia it yields the thiocarbamide,  $\text{CS}(\text{NH.CMe}_3).\text{NH}_3$ , crystallising in prisms, and very soluble in alcohol; it melts at  $165^\circ$ . By the action of trimethylcarbinamine on the thiocarbimide, di-isobutyl thiocarbamide,  $\text{CS}(\text{NH.CMe}_3)_2$ , is formed, which is also obtained by heating the compound



with alcohol. It is soluble in water, alcohol, and ether, and melts at  $162^\circ$ .

*Tertiary amylthiocarbamide*,  $\text{CMe}_2\text{Et.NCS}$ .—The salt of the thiocarbamine, obtained by the action of carbon bisulphide on the amine  $\text{CMe}_2\text{Et.NH}_2$ , when treated with mercuric chloride, yields tertiary amyl thiocarbimide. It is a liquid boiling at  $166^\circ$ , and having a pleasant odour. L. T. O'S.

**Crystalline Form of Nitrosothymol, Lapachic Acid, and Cuminic Acid.** By R. PAVERIANCO (*Gazzetta*, 10, 78—82).—*Nitrosothymol*,  $\text{C}_8\text{H}_7\text{Me}(\text{C}_6\text{H}_5)(\text{NO}).\text{OH}$ .—This was prepared from the synthetic thymol obtained from cumic alcohol cumene, and from camphor cymene, the compounds from the two sources being identical. The crystals are monoclinic  $a : b : c = 1.9874 : 1 : 0.8941$ ,  $\eta = 94^\circ 57' 20''$ . Observed forms 100, 010, 001, 101,  $\bar{1}01$ , 110; observed combinations 100 010 with the cleavage plane  $\bar{1}01$ , and the same with 110; 100 010  $\bar{1}01$  101; the same with 001. Cleavage parallel to  $\bar{1}01$ . Twin plane parallel to 100. Positive double refraction  $2H_e = 86^\circ 10'$  for the red and  $82^\circ 20'$  for the violet. The colour of the crystals is straw-yellow.

*Lapachic acid* belongs to the monoclinic system.  $a : b : c =$

0.7206 : 1 : 0.6492;  $\eta = 97^\circ 9'$ . Observed forms 100, 001, 101,  $\bar{1}01$ , 110, 130, 150,  $\bar{1}33$ , 133,  $h\ 3h\ l$ . Observed combinations 100 001 101  $\bar{1}01$  150, the same with 110 130  $\bar{1}33$  133. Cleavage takes place easily parallel to 100. The twin plane is parallel to 100.

*Cumic Isopropylbenzoic Acid*,  $C_6H_4(CH_2.CH_2.Me).COOH$ .—The crystals belong to the triclinic system  $a : b : c = 2.07825 : 1 : 1.34669$  :—

|          |                  |         |                        |
|----------|------------------|---------|------------------------|
| $c$      | $= 73^\circ 21'$ | $\xi$   | $= 103^\circ 13'$      |
| $\beta$  | $= 75^\circ 8'$  | $\eta$  | $= 100^\circ 50'$      |
| $\gamma$ | $= 72^\circ 56'$ | $\zeta$ | $= 103^\circ 44' 30''$ |

Observed forms 100, 001, 010, 110,  $\bar{1}01$ ,  $\bar{4}70$ ,  $20\bar{1}$ . Observed combinations 100 001 110 110  $\bar{4}70$ , the same with 010 and with 010  $20\bar{1}$ . Cleavage plane parallel to 100 imperfect. The crystals are colourless, and usually have the form 100 greatly developed. C. E. G.

**Nitration of Paranitrobenzoic Acid.** By H. HÜSNER and A. STROMEYER (*Ber.*, 13, 461—462).—Paraorthodinitrobenzoic acid, described by Tiemann and Judson (*Ber.*, 3, 232), and by Griess (*ibid.*, 7, 1223), can also be obtained by saturating a mixture of fuming nitric and sulphuric acids with paranitrobenzoic acid. The solution is warmed on a water-bath and afterwards heated at  $170^\circ$  for 12 hours, the unchanged paranitrobenzoic acid is precipitated by diluting the mixture with water. Soda is added to the filtrate until a fourth of the acid present is neutralised; the liquid is evaporated to dryness, and the residue extracted with alcohol. From the alcoholic solution barium nitrobenzoate is prepared, from which the lead salt and the free acid can be derived. W. C. W.

**$\gamma$ -Sulphoisophthalic Acid and the Corresponding  $\gamma$ -Hydroxyisophthalic Acid.** By K. HEINE (*Ber.*, 13, 491—497).— $\gamma$ -Sulphoisophthalic acid,  $C_6H_3(SO_3H)(COOH)(COOH) = [1 : 3 : 5]$ , prepared by heating a mixture of sulphuric anhydride and isophthalic acid, and purified by conversion into its barium and lead salts, is a thick uncrystallisable syrup. It forms three potassium salts; the normal salt,  $C_6H_3K_3SO_7$ , crystallises in needles, which are very soluble in water. A solution of this substance in hot hydrochloric acid deposits beautiful needles of the mono-potassium salt,  $C_6H_4KSO_7 + 3H_2O$ , on cooling. The crystals are insoluble in alcohol and ether; they dissolve freely in hot and sparingly in cold water.  $C_6H_4K_2SO_7$  crystallises in long prisms. The salts of  $\gamma$ -sulphoisophthalic acid, with the exception of lead sulphoisophthalate, are soluble in water.

Trimesic acid appears to be produced by fusing together  $\gamma$ -potassium formate and  $\gamma$ -sulphoisophthalate.

$\gamma$ -Hydroxyisophthalic acid,  $C_6H_3(OH)(COOH)(COOH) = [1 : 3 : 5]$ , is formed by fusing the mono-potassium  $\gamma$ -sulphoisophthalate with 10 times its weight of potash for five minutes. By dissolving the product in water and acidifying the solution with hydrochloric acid, the new acid is obtained as a colourless crystalline deposit, which melts at  $285^\circ$ , and begins to sublime at the same temperature. If the fusion is carried on too long,  $\alpha$ -hydroxyphthalic acid is produced.

The  $\gamma$ -acid contains 2 mols. of water of crystallisation which are



expelled at 100°. It forms three series of salts:  $C_6H_4AgO_5$  is deposited in slender needles when silver nitrate is added to a hot aqueous solution of the acid:  $C_6H_4Ag_2O_5$  is thrown down as an insoluble crystalline precipitate, when silver nitrate is added to the corresponding ammonium salt. Calcium chloride does not produce a precipitate in neutral solutions of the acid, but on addition of ammonia,  $(C_6H_4O_5)_2Ca$  separates out. Barium chloride yields an immediate precipitate with the alkaline solution, and when added to a hot neutral solution a white salt is formed, which is deposited in needle-shaped crystals from the liquid on cooling. Lead nitrate produces a white precipitate in neutral solutions.

Diethyl  $\gamma$ -hydroxyisophthalate,  $C_6H_3(OH)(COOEt)_3$ , crystallises in monoclinic prisms, which melt at 103°; the dimethyl salt forms needle-shaped crystals (m. p. 159–160°). The following table exhibits the points of difference between the three isomeric hydroxyisophthalic acids:—

|                          | $\alpha$ .        | $\beta$ .                            | $\gamma$ .         |
|--------------------------|-------------------|--------------------------------------|--------------------|
| Water of crystallisation | None .....        | 1 molecule.....                      | 2 molecules        |
| Melting point .....      | Above 300° .. {   | Anhydrous, 243°<br>Air dried, 239°.. | } 284–285°         |
| Solubility in hot water. | Freely .....      | Freely .....                         | Sparingly          |
| Aqueous solution.....    | Non-fluorescent.  | Fluorescent ....                     | Non-fluorescent    |
| Ferric chloride.....     | Red coloration .. | Red coloration ..                    | No change          |
| Neutral barium salt....  | Very soluble....  | Insoluble .....                      | Sparingly soluble  |
| Diethyl salt .....       | Melting point 52° | —                                    | Melting point 103° |

W. C. W.

**Acetobenzoic Anhydride.** By W. H. GREENE (*Bull. Soc. Chim.* [2], 33, 424–426).—On repeating the experiments of Loir (this vol., 31) on the action of hydrochloric acid and chlorine on acetobenzoic anhydride, the author finds that it behaves in a precisely similar manner, whether the anhydride is prepared from acetic chloride and sodium benzoate or from benzoic chloride and sodium acetate. By treating the anhydride with hydrochloric acid at a temperature below 100° the liquid solidifies; between 55° and 60°, acetic chloride distils over, the distillate which comes over below 120° contains acetic chloride and acetic acid, and by heating the residue more strongly, and increasing the current of hydrochloric acid, a small quantity of benzoic chloride distils over, and it is also found in the residue.

By passing hydrochloric acid into acetobenzoic anhydride in the cold, the liquid solidifies, and consists of acetic chloride, acetic acid, benzoic chloride, and benzoic acid. With chlorine, acetobenzoic anhydride, prepared by either method, gave the same products of decomposition, namely, acetic chloride, monochloroacetic acid, benzoic chloride, and monochlorobenzoic acid. If the reaction takes place between 140° and 155° the two first bodies are the principal products. There is some difficulty in separating the chloroacetic acid and benzoic chloride, owing to the boiling points being nearly the same. These results

prove the identity of the so-called acetylbenzoic anhydride, and the benzoylacetic anhydride of Loir.

L. T. O'S.

**Digallic Acid.** By H. SCHIFF (*Ber.*, 13, 454—457).—In replying to Freda's criticisms (*Gazzetta*, 9, 327, and *Ber.*, 12, 1576), the author points out that when sulphuretted hydrogen is passed through a hot solution of natural or artificial digallic acid, decomposition may take place in two different ways, viz., that either the digallic acid is simply converted into gallic acid or sulphur separates out and another acid is formed in addition to the gallic acid.

Artificial digallic acid is more easily decomposed by sulphuretted hydrogen, than tannin containing 3 per cent. of glucose.

Hot alcoholic or aqueous solutions of gallic acid can dissolve small quantities of arsenic sulphide. No change occurs when the liquid is boiled.

W. C. W.

**Chemical Constituents of Stereocaulon Vesuvianum.** By E. PATERNO (*Gazzetta*, 10, 157).—The author states that by exhausting this lichen with ether he obtained a colourless crystalline compound, which after purification by crystallising it from chloroform, appeared to be identical with atranoric acid,  $C_{19}H_{16}O_8$ , from *lecanora utra*. Coppola (this vol., 382), found nothing but succinic acid, and although it is possible that this acid may be present as some salt insoluble in ether, the fact remains that Coppola missed the principal constituent of the lichen.

C. E. G.

**Homofluorescein, a new Colouring Matter from Orcinol.** By H. SCHWARZ (*Ber.*, 13, 543—568).—*Sodium homofluorescein*, prepared by gently boiling 10 grams of orcinol dissolved in 20 c.c. of a saturated solution of common salt, with 8 grams of chloroform, and 80 c.c. of a 10 per cent. solution of soda. The liquid soon acquires a red colour, and after boiling for 10 minutes begins to deposit red needle-shaped crystals. A second crop of crystals can be obtained by boiling the mother-liquor with chloroform and soda.

The aqueous or alcoholic solution of the salt has a reddish-yellow colour. 1 mgrm. imparts a pale yellow colour, and a green fluorescence to a liter of water. The silver salt is thrown down as a dark red precipitate when silver nitrate is added to a solution of sodium homofluorescein.

When a concentrated aqueous solution of the sodium compound is boiled with 150 parts of glacial acetic acid, dark red crystals having a green metallic lustre are deposited, which, when heated at  $100^\circ$ , lose 32 per cent. of acetic acid and leave pure homofluorescein,  $C_{23}H_{18}O_8$ . This compound dissolves sparingly in water, alcohol, and cold acetic acid, and it combines with the alkalis and alkaline earths to form fluorescent solutions, which deposit red needle-shaped crystals on evaporation. The ammonium salt is very unstable, splitting up at the ordinary temperature into ammonia and homofluorescein. The barium salt,  $C_{23}H_{18}BaO_8 + 3H_2O$ , crystallises in brownish-red needles or scales which exhibit a golden lustre.

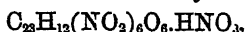
The salts of the heavy metals are insoluble in water.

The fluorescence of homofluorescein is destroyed by reduction with sodium amalgam, and also by oxidation with potassium permanganate or dichromate.

*Tetra-* and *hexa-bromohomoeosin* are produced by adding the calculated amount of bromine mixed with hot acetic acid to a boiling solution of sodium homofluorescein in alcohol or glacial acetic acid. The alcoholic solution of these compounds has a cherry-red colour and a pale yellow fluorescence. Tetrabromohomoeosin,  $C_{23}H_{14}Br_4O_6$ , forms a pale red crystalline sodium salt,  $C_{23}H_{13}NaBr_4O_6 + 4H_2O$ .

On adding a solution of iodine in potassium iodide to an aqueous solution of sodium-homofluorescein, a black precipitate is deposited, which turns red when heated. It consists of *tri-iodohomoeosin*,  $C_{23}H_{15}I_3O_6$ . The *sodium salt* is a red crystalline body, dissolving in alcohol or water, forming a cherry-red liquid which is not fluorescent. With acetic anhydride, homofluorescein yields a resinous compound having the composition,  $C_{23}H_{21}Ac_4O_5 + 2H_2O$  or  $C_{23}H_{16}O_5 + 2C_4H_6O_3$ . On addition of water to the alcoholic solution of this substance, a brown syrup separates out, which solidifies, forming brownish-yellow crystalline plates.

Warm nitric acid (sp. gr. 1.4) dissolves sodium homofluorescein, but the liquid rapidly deposits *hexanitromonoxyhomofluorescein nitrate*,



as a yellowish-red crystalline powder, which explodes without melting at  $180^\circ$ . The nitrate is soluble in alcohol, but is decomposed by water into hexanitrohomofluorescein and nitric acid. The nitro product is less soluble in nitric acid than in water, and it may be obtained in golden-coloured rhombic plates having the composition—



by adding dilute nitric acid to the hot aqueous solution. The sodium salt,  $C_{23}H_{11}(NO_2)_6NaO_6$ , and the silver salt,  $C_{23}H_{11}(NO_2)_6AgO_6$ , crystallise in glistening red plates.

*Diammonium pentanitrodiazamidomonoxyhomofluorescein* is deposited in red or yellow crystalline plates when a solution of the preceding nitro-product in boiling ammonia is acidified with acetic acid. From this compound the *tri-* and the *di-potassium salts*,  $C_{23}H_{11}K_3N_6O_{18}$  and  $C_{23}H_{12}K_2N_6O_{18}$ , were prepared: the former resembles potassium picrate in appearance, the latter forms pale yellow crystals.

*Hexamidooxyfluorescein hydrochloride*,  $C_{23}H_{12}(NH_2)_6O_6 + HCl + H_2O$ , prepared by the reduction of the nitro-compound with tin and hydrochloric acid, forms transparent colourless crystals, which readily lose hydrochloric acid and acquire a brown colour. If the reduction is carried on in an alkaline solution an intense purple colour is produced.

When treated with a warm aqueous solution of potassium cyanide the hexanitromonoxyhomofluorescein yields hexanitrohomofluorescein-cyamic acid.

W. C. W.

**Xylene Derivatives.** By R. NIETZKI (*Ber.*, 13, 470—473).—*Amidoazoxylene*, prepared by treating xyldine with nitrous acid, *crys-*

tallises in orange-coloured plates (m. p.  $115^{\circ}$ ); it dissolves in alcohol and ether, forming dark yellow solutions which are changed to carmine colour by the addition of an acid in excess. The hydrochloride forms red needles, soluble in alcohol. It is decomposed by water. On reduction with zinc and hydrochloric acid, *paraxylenediamine* is produced together with xylydine. The crude product is made alkaline and extracted with ether, and that portion of the residue (remaining after evaporating off the ether) which boils at  $270-300^{\circ}$  is recrystallised from hot benzene. In this way *paraxylenediamine* is obtained in colourless needles (m. p.  $150^{\circ}$ ), soluble in alcohol and in hot water. The salts of this base are very soluble.

*Xyloquinone*,  $C_8H_6O_2$ , formed by the oxidation of xylenediamine or xylydene melts at  $125^{\circ}$ , and sublimes even at the ordinary temperature, producing golden-yellow needles. It bears a strong resemblance to its lower homologues, and is perhaps identical with the metaphloron of Rommier and Bonilhon (*Compt. rend.*, 55, 214).

*Xyloquinol*, prepared by treating xyloquinone with warm sulphurous acid solution, is deposited from a hot aqueous solution in silvery plates (m. p.  $212^{\circ}$ ). It is converted into the quinone by oxidation. Xyloquinone combines with hydrochloric acid, forming monochloroxyloquinol.

W. C. W.

**Constitution of Rosaniline Salts.** By A. ROSENSTIEHL (*Bull. Soc. Chim.* [2], 33, 342-349 and 426-435).—E. and O. Fischer (*Annalen*, 194, 285) have shown that *paraleucaniline* is the triamido-derivative of diphenylmethane, the amido-groups being equally divided among the phenyl-groups, and moreover *pararosaniline* bears the same relation to *paraleucaniline* that triphenylcarbinol does to triphenylmethane.

Triphenylmethane.



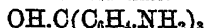
Triphenylcarbinol.



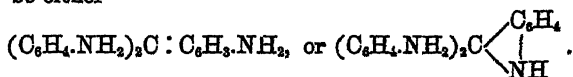
Paraleucaniline.



Pararosaniline.

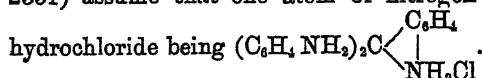


In discussing the constitution of the salts of rosaniline, they show that the base loses the elements of water when it combines with an acid, and this separation of water they conclude is accompanied by a rearrangement of the atoms. The formula they give for the combined base may be either—



Of these they prefer the latter, since the former formula would make rosaniline to be a derivative of the hydrocarbon,  $Ph_3C : C_6H_5$ , which does not exist. There is therefore one formula for the uncombined base, and another for the combined, and according to the formula,  $C_{18}H_{17}N_3$ , for *pararosaniline*, it contains two atoms of hydrogen less than *paraleucaniline*, whereas in reality it contains the same number of hydrogen atoms, and differs by an atom of oxygen. In the formation of the salts from the base,  $C_{18}H_{17}N_3$ , E. and O. Fischer (*Ber.*, 12,

2351) assume that one atom of nitrogen becomes pentatonic, the



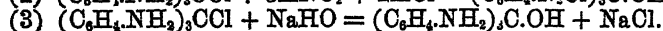
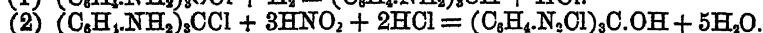
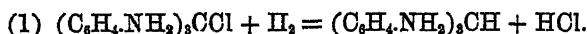
Starting with pararosanine hydrochloride having the above formula, the formation of paralencanine, the diazo-derivative and the base from it are all attended with a rearrangement of the aromatic group, the double linking of the nitrogen atom being in each case broken,

and an amido-group formed. If  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{NH}_2\text{Cl} \end{array}$ , is the con-

stitution of pararosanine hydrochloride, then  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{NH}.\text{OH} \end{array}$

would be the base, and it is no longer a tertiary alcohol, but if the base is a carbinol,  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C}(\text{OH}).\text{C}_6\text{H}_4.\text{NH}_2$ , then the chloride should be represented thus:  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{CCl}.\text{C}_6\text{H}_4.\text{NH}_2$ , as the haloid ether of a tertiary amido-alcohol. The reactions can, by the above formula, be explained without any alteration in the grouping of the atoms.

The formation of (1) paralencanine, (2) the diazo-derivatives, and (3) the base from the hydrochloride, may be represented as follows:—



That the substitution of the alcoholic OH group by chlorine, and *vice versa*, is not a new function of these bodies, is seen by the formation of methyl chloride and benzyl chloride, and notably triphenylchloromethane, which is so unstable as to be decomposed by the moisture in the atmosphere; it is also readily reduced by hydrogen. The question of the group,  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C}$ , playing the part of an electropositive element, only needs reference to the reaction of nitroform with potash, forming  $(\text{NO}_2)_3\text{C.K}$ , in which the nitro-group  $(\text{NO}_2)_3\text{C}$  plays the part of an electronegative element; such being the case, it is not impossible that the amido-group,  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C}$ , should play the part of an electropositive element.

Leucanine forms a series of triacid salts, each of the groups  $(\text{C}_6\text{H}_4.\text{NH}_2)$  acting as a primary amine, and uniting with one molecule of a monobasic acid, paralencanine hydrochloride being—



Pararosanine ought to form two series of salts, the monacid salts and the series corresponding with the chloride  $(\text{C}_6\text{H}_4.\text{NH}_2\text{Cl})_3\text{CCl}$ . This is in accordance with fact and with the views of Hofmann, although he considered the polyacid salts as triacid, based on his analyses, which were only approximative owing to the instability of the salts, and on his idea that rosaniline was a triamine. Pararosanine therefore as a carbinol forms two series of salts, (1) ethers of a tertiary,

aromatic amido-alcohol, and (2) salts of the ether, which is a triacid amine.

In explaining the constitution of malachite-green, E. and O. Fischer have again resorted to the double linking of the nitrogen atom when the base is combined. At first they proposed for the combined base

the formula, 
$$\begin{array}{c} \text{Me}_2\text{N.C}_6\text{H}_4 \\ \text{Ph} \quad \diagup \quad \text{C} \quad \diagdown \quad \text{C}_6\text{H}_4 \\ \quad \quad \quad | \\ \quad \quad \quad \text{NMe} \end{array}$$
, on the assumption that formyl aldehyde was formed when the leuco base is oxidised, this being denied by

Doebner: they suggest the formula,

$$\begin{array}{c} \text{Ph} \quad \diagup \quad \text{C} \quad \diagdown \quad \text{C}_6\text{H}_4 \\ \text{Me}_2\text{N.C}_6\text{H}_4 \quad \quad | \\ \quad \quad \quad \text{N} \begin{array}{l} \diagdown \text{CH}_2 \\ \diagup \text{CH}_2 \end{array} \end{array}$$
, which

is derived from the carbinol,  $\text{PhC(OH)(C}_6\text{H}_4\text{.NMe}_2)_2$ , by the hydroxyl uniting with an atom of hydrogen of one of the methyl groups leaving the unsaturated link of the carbon of the methane to unite with the nitrogen (which becomes pentavalent) of the group  $\text{C}_6\text{H}_4\text{.NMe}$ , thus formed. When this base unites with an acid, the hydrogen of the acid unites with the group  $\text{CH}_2$ , forming methyl, and the acid radicle saturates the vacant nitrogen link, the hydrochloride being

$$\begin{array}{c} \text{Ph} \quad \diagup \quad \text{C} \quad \diagdown \quad \text{C}_6\text{H}_4 \\ \text{Me}_2\text{N.C}_6\text{H}_4 \quad \quad | \\ \quad \quad \quad \text{NMe}_2\text{Cl} \end{array}$$
. A body having such a formula belongs to

the class of quaternary ammonium compounds, in which the chlorine is only replaced by OH with great difficulty. In this case, however, the change is easily effected. To meet this objection, E. and O. Fischer assume that since the nitrogen is united to triphenylcarbinol, it has special properties, and that the reaction takes place in two stages, the

ammonium hydroxide, 
$$\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C} \\ | \\ \text{NMe}_2\text{.OH} \end{array}$$
, which readily undergoes molecular change, the double link breaking up, and the result being the carbinol  $\text{:C(OH).C}_6\text{H}_4\text{.NMe}_2$ .

Starting with that formula for malachite-green, the author explains the above reactions on the same principle as he does the constitution of the pararosaniline salts, namely, by considering the salts as ethers of the carbinol. Thus malachite-green hydrochloride is—



By so doing, the formation of a hypothetical base is not necessary, and the nitrogen in the salts derived from both bases has the same properties, which is not the case according to the views of E. and O. Fischer, in the one case nitrogen being trivalent, and in the other pentavalent.

Regarding E. and O. Fischer's views on the identity of the violet from methylaniline and Hofmann's violet, the author does not consider the evidence in support of them conclusive, but maintains rather that the violet from methylaniline would be—



whilst Hofmann's violet from pararosaniline would be—

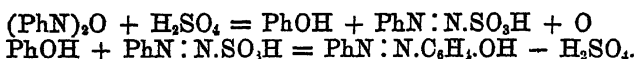


To establish their identity, a molecular change would be necessary.

Discussing the theory of the double linking of the atoms and its bearing on the colour of bodies, the author maintains that the views of Graebe and Liebermann (*Ber.*, 1, 106, 1868) have not been confirmed, for since the constitution of anthracene is fully established, the cause of the coloration of the anthraquinones cannot be due to double linking. Again, there are nitroform, the nitroanilines, and the nitrophenols, colouring matters which have no double linking.

L. T. O'S.

**Conversion of Azoxybenzene into Oxyazobenzene.** By O. WALLACH and L. BELLI (*Ber.*, 13, 525—527).—When water is added to a solution of azoxybenzene in warm sulphuric acid, unaltered azoxybenzene and an isomeride are precipitated. The new compound crystallises in red pyramids, which have a metallic lustre, and appears to be identical with the oxyazobenzene of Griess (*Ber.*, 3, 233). The formation of this substance is probably due to the following reactions:—



W. C. W.

**Nitration of Salicylanilide.** By C. MENSCHING (*Ber.*, 13, 462—463).—*α-Nitrosalicylanilide* (m. p. 224°) produced by the action of nitric acid on salicylanilide, is converted into *α*-metanitrosalicylic acid by treatment with alkalis.

*Salicylorthonitranilide*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH.CO.C}_6\text{H}_4.\text{OH}$ , obtained by the action of phosphorous chloride on a mixture of orthonitraniline and salicylic acid, crystallises in yellow plates, which dissolve freely in benzene, but are only sparingly soluble in petroleum and in alcohol.

Nascent hydrogen converts salicylorthonitranilide into an anhydro-

compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C.C}_6\text{H}_4.\text{OH}$ , which forms colourless needle-shaped crystals (m. p. 222.5°), readily soluble in ether and alcohol. This substance combines with acids forming colourless salts.

W. C. W.

**Thiamides.** By O. WALLACH (*Ber.*, 13, 527—530).—The sodium compounds of the *isothiamides*,  $\text{SR}''.\text{R.C:NR}'$  are easily obtained in colourless glistening crystalline plates by adding ether to a mixture of a concentrated alcoholic solution of the thiamide (1 mol.) with a freshly prepared concentrated alcoholic solution of sodium (1 atom). The sodium compounds dissolve freely in water. When carbonic anhydride is passed through the aqueous solution, the thiamide is deposited in a state of purity.

Sodium thiacetanilide exhibits the following reactions. It produces with silver nitrate a black, with lead acetate a white precipitate, which turns black on boiling, with copper sulphate a yellowish-green, with

mercuric chloride a white precipitate, which changes to yellow when boiled, with mercurous nitrate dark brown, ferric chloride white, and with cobalt nitrate a greenish-white precipitate.

*Methylisothiacetanilide*,  $\text{SMe.MeC:NPh}$ , prepared by the action of methyl iodide and sodium on thiacetanilide, boils at  $244\text{--}246^\circ$ . *Thiacetmethylanilide*,  $\text{SMe.CNMePh}$ , from acetmonomethylanilide, crystallises in colourless monoclinic plates soluble in ether, chloroform, and alcohol. This compound melts at  $58\text{--}59^\circ$ , and boils at  $290^\circ$ . The two isomerides, thiaceotorthotoluidide and thiaceotparatoluidide, melt at  $67^\circ$  and  $130^\circ$  respectively.

The isothiamides combine with the iodides of alcoholic radicles at the ordinary temperature, forming a crystalline mass.

W. C. W.

**Orthochlorobenzparatoluide and its Derivatives.** By H. SCHREIB (*Ber.*, 13, 465—468).—By the action of orthochlorobenzoic chloride on paratoluidine, colourless crystals of *orthochlorobenzparatoluide* are obtained. This compound melts at  $131^\circ$ , dissolves freely in alcohol, and yields several nitro-products.

*Orthochlorobenzmetanitroparatoluide* prepared by dropping the preceding compound into a mixture of 1 part of fuming and 3 parts of concentrated nitric acid, forms yellowish-green crystals (m. p.  $139^\circ$ ) soluble in glacial acetic acid. It yields metanitrotoluidine on decomposition with alcoholic potash.

*Dinitro-orthochlorobenzparatoluide*, obtained by treating the mononitro-derivative with hot fuming nitric acid, forms colourless silky crystals (m. p.  $228^\circ$ ), soluble in chloroform and in glacial acetic acid.

The trinitro-product,  $\text{C}_{14}\text{H}_9\text{N}_4\text{O}_7\text{Cl}$  (m. p.  $239^\circ$ ) is prepared by heating a solution of orthochlorobenzparatoluide in fuming nitric acid, and resembles the preceding compound.

*Orthochlorobenzamidoparatoluide* (m. p.  $153^\circ$ ) is formed by the reduction of the mononitro-derivative by tin and glacial acetic acid saturated with gaseous hydrochloric acid. When an aqueous solution of hydrochloric acid is used, chlorobenzoic acid and diamidotoluene are produced. The amido-compound is soluble in alcohol.

By the action of benzoic chloride on the preceding substance, colourless needles (m. p.  $178^\circ$ ) are obtained, which have the composition,  $\text{C}_6\text{H}_5\text{Me.NHCOPh.NHCO.C}_6\text{H}_4\text{Cl}$ . This base yields on distillation *anhydro-orthochlorobenzmetamidoparatoluide*,  $\text{C}_6\text{H}_5\text{Me.N:C(NH).C}_6\text{H}_4\text{Cl}$ .  
W. C. W.

**Action of Alcohols and Phenols on Acid Imide Chlorides.** By O. WALLACH and A. LIEBMANN (*Ber.*, 13, 506—511).—If oxamethane chloride,  $\text{COOEt.CCl}_2\text{.NH}_2$ , is covered with an equivalent quantity of benzyl alcohol, it dissolves in the alcohol, and a sudden evolution of ethyl chloride and hydrochloric acid takes place. The mixture on cooling deposits white needle-shaped crystals (m. p.  $135^\circ$ ), which have the composition  $\text{NH}_2\text{.CO.COO.CH}_2\text{Ph}$ .

Oxamethane chloride yields similar compounds with isobutaldehyde, fermentation amyl alcohol and anhydrous phenyl, viz.:

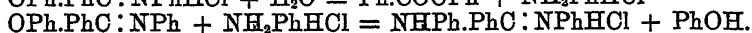
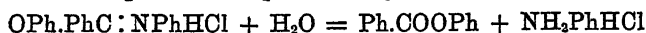
$\text{NH}_2\text{.CO.COO.C}_4\text{H}_9$  (m. p.  $90^\circ$ ),  $\text{NH}_2\text{.CO.COO.C}_6\text{H}_5$  (m. p.  $93^\circ$ ),



and  $\text{NH}_2\text{CO.COOPh}$  (m. p.  $132^\circ$ ). The first of these three compounds is also produced by saponifying isobutyl oxalate with ammonia.

By heating together phenol and benzanilidimide chloride, a green syrupy liquid is obtained, which solidifies in a few days to a yellow mass (m. p. above  $260^\circ$ ) insoluble in ether, chloroform, and benzene. On exposure to moist air, it rapidly decomposes into phenol, phenyl benzoate, benzenyldiphenylamidine hydrochloride, and aniline hydrochloride. If the syrupy liquid is protected from the influence of moisture by immersion in anhydrous ether, it is found to have the composition  $\text{OPh.PhC:NPh.HCl}$ .

Its decomposition is represented by the following equations:—



W. C. W.

**Synthesis of Phosphenyl Sulphochloride.** By H. KÖHLER (*Ber.*, 13, 463—464).—Phosphenyl sulphochloride can easily be prepared by allowing sulphur chloride to drop slowly into a flask (fitted with an upright condenser) containing phosphenyl chloride,  $3\text{PhPCl}_2 + \text{S}_2\text{Cl}_2 = 2\text{PhPCl}_2\text{S} + \text{PhPCl}_4$ .

When the reaction is complete, the flask is cooled down in a freezing mixture, which causes phosphenyl tetrachloride to crystallise out. The liquid portion of the product is shaken up with water, dried, and rectified; the phosphenyl sulphochloride boils at  $270^\circ$ .

W. C. W.

**Action of Bromine on Diphenylmethane.** By C. FRIEDEL and M. BALSCHN (*Bull. Soc. Chim.* [2], 33, 337—342).—Diphenylmethane, prepared by the action of benzoic chloride on benzene in presence of aluminium chloride, when treated with 2 mols. of bromine, yields *diphenyldibromomethane*,  $\text{CBr}_2\text{Ph}_2$ , a brown liquid which solidifies on standing. It is decomposed by repeated distillation or by continued heating, being converted into a crystalline solid (m. p.  $214^\circ$ ) containing 4 per cent. of bromine, which is obtained in orthorhombic plates when heated at  $150^\circ$  with alcohol under pressure. It consists of impure *tetraphenylethylene*,  $\text{Ph}_2\text{C:CPh}_2$ , from which the pure substance may be obtained by treating the solution of it in toluene with sodium for some time.

When heated with water at  $150^\circ$  for some time, diphenyldibromomethane is in great part converted into benzophenone.

*Diphenylmonobromomethane*,  $\text{CHBrPh}_2$ , (m. p.  $45^\circ$ ).—By the action of 1 mol. bromine on 1 mol. diphenylmethane, a brown liquid is obtained, from which crystals of the monobromo-compound separate on cooling; it is very soluble in benzene. By the action of alcoholic potash, the bromo-compound is converted in the ethyl ether of diphenylcarbinol,  $\text{CHPh}_2\text{OEt}$ , an oily liquid boiling at  $288^\circ$ . Linne-mann (*Annalen*, 133, 17) obtained the same body by the action of sulphuric acid on a mixture of benzhydrol (diphenylcarbinol) and alcohol, and describes it as a liquid boiling at  $183^\circ$ , and turning green when exposed to the light; that prepared by the authors is not affected by sunlight. The same ether is obtained by the continued boiling of the bromo-compound with alcohol.

The amyl ether is obtained by the action of amyl alcohol and potash on diphenylmonobromomethane. It is an oily colourless liquid (b. p.  $310^{\circ}$ ).

Diphenylmethylacetate,  $\text{CHPh}_2\text{O}\cdot\text{Ac}$ , is obtained as a liquid (b. p.  $310^{\circ}$ ) by treating the bromo-compound with potassium acetate. The continued action of alcoholic potash on the acetate converts it into diphenylcarbinol,  $\text{CHPh}_2\text{OH}$  (m. p.  $65^{\circ}$ ).

When heated with water at  $150^{\circ}$  for some time, diphenylmonobromomethane yields diphenylcarbinol and the corresponding ether. The latter is sparingly soluble in alcohol, from which it crystallises in small prisms. It melts at  $110^{\circ}$  (Linneman,  $118^{\circ}$ ), and on cooling remains liquid at temperatures much below its melting point; it finally solidifies to an opaque crystalline mass, which melts at the original temperature. The ether crystallises in anorthic prisms from its solution in a mixture of alcohol and benzene.

Diphenylcarbinol is obtained in fine needles by adding water to the mother-liquors of the ether.

Diphenylmonobromomethane is gradually converted into the carbinol by contact with water at the ordinary temperature.

L. T. O'S.

**A New Colouring Matter.** By W. v. MILLER (*Ber.*, 13, 542—543).—"Biebrich Scarlet" is a mixture of "mandarine yellow" with several red colouring matters, two of which proved to be the di- and trisulphonic acids of the compound  $\text{PhN} : \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N} : \text{N}\cdot\text{C}_{10}\text{H}_7\cdot\text{OH}$ .

W. C. W.

**Lævorotary Terebenthene from French Turpentine Oil.** By F. FLAVITZKY (*Bull. Soc. Chim.* [2], 33, 296).—This terebenthene yields hydrate of terebenthene not only when treated with nitric acid, but also with sulphuric or hydrochloric acid. The reaction takes place more quickly when hydrochloric acid is used than with either of the other acids. By treating lævorotary terebenthene with alcohol and sulphuric acid (sp. gr. 1.64), the rotary power disappears, and a substance boiling at  $175^{\circ}$  is obtained, probably an isomeride.

L. T. O'S.

**Adipic Acid from Camphor.** By J. KACHLER (*Ber.*, 13, 487—488).—Camphor yields on oxidation with chromic or nitric acid, camphoronic acid,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , hydro-oxycamphoronic acid,  $\text{C}_{10}\text{H}_{14}\text{O}_8$ , and some syrupy acids which were not investigated. This confirms the accuracy of the author's former experiments (*Annalen*, 200, 340), but does not agree with Ballo's observation (*Ber.*, 12, 1597, and this vol., p. 50) that adipic acid is formed when camphor is oxidised with chromic acid.

W. C. W.

**Resin from Rosewood.** By A. TEBREIL and A. WOLFF (*Bull. Soc. Chim.* [2], 33, 435—436).—The resin obtained from rosewood has a brilliant black colour with a brown reflection, a vitreous fracture, and a balsamic odour; its sp. gr. at  $15^{\circ}$  is 1.2662, and it melts at  $95^{\circ}$ . It dissolves in all proportions in alcohol, but is less soluble in ether, chloroform, and carbon bisulphide, and is insoluble in water.

Soda and potash dissolve the resin, forming brown-coloured solutions, from which it is again separated in brown flakes on adding an acid;

on boiling the solution an odour resembling benzaldehyde and hawthorn is evolved. Sulphuric acid also dissolves the resin with a blood-red colour; by adding water, the resin is precipitated without alteration. When treated with nitric acid, it yields an acid of an orange colour crystallising in needles.

On distillation, white vapours are evolved at first, having an odour resembling those from gum benzoin, but containing no benzoic acid, then an essential oil passes over, and finally tarry matters. Its analysis corresponds with the formula  $C_{21}H_{21}O_6$ ; it forms salts with lead and barium.

By extracting other coloured woods, such as amaranth wood, iron wood, ebony, &c., with alcohol, resins resembling that from rosewood are obtained, but not in so large a proportion; rosewood yields 35 per cent. of its weight of resin.

L. T. O'S.

**Chlorophyll.** By PRINGSHEIN (*Compt. rend.*, 90, 161—165).—By exposing a portion of vegetable tissue under the microscope to bright sunlight concentrated by means of a large lens, the author has been able to follow by direct observation the effects of light on chlorophyll, and on the protoplasmic contents of the living cell. In this manner he has proved the existence in chlorophyll of a colourless, crystallisable, oleaginous substance, hitherto unknown, which appears to have a direct relation with the assimilation of carbon by the green parts of plants. This substance, named *hypochlorin*, has not been isolated in a pure condition, but it has been shown to be the only carbon compound, in phanerogams at least, which cannot be formed without the aid of light.

Researches on chlorophyll itself have fairly proved that this pigment is not decomposed in the act of carbon assimilation, and that it cannot be considered as the mother-substance of all or any of the carbon compounds found in plants.

It is true that its decomposition in the isolated cell can be directly observed, but this decomposition is due to the action of oxygen, and is quite independent of absorption of carbonic anhydride, or even of the presence of this gas.

The author's micro-photochemical researches on the green cell show that respiration or inspiration of oxygen increases in a corresponding ratio with the intensity of the light, and that this absorption may become so great as to be positively injurious to the plant; the energy of oxidation becomes then greater than the energy of assimilation, the hypochlorin disappears, and the other combustible substances which together make up the contents of the cell, are rapidly oxidised and destroyed. But the chlorophyll by its power of luminous absorption counterbalances these two functions; it acts as a protective screen, absorbing the chemical rays and diminishing respiration, thereby enabling the assimilation of carbon by the plant to keep pace with the oxidation of its carbon compounds.

When the particles of chlorophyll are examined carefully under the microscope they are seen to be porous bodies, the solid portion of which, like a sponge, is impregnated throughout with an oil, in which the green pigment is dissolved, and which generally contains the

crystallisable substance termed hypochlorin. Protected by the coloured pigment, the hypochlorin, which appears to be the mother-substance of the carbohydrates, does not undergo rapid combustion, but either remains unaltered in the chlorophyll, or suffers only a regulated oxidation, such as may be properly said to be one of the life functions of the plant; in concentrated solar light, however, the hypochlorin is instantly destroyed before even the chlorophyll has had time to be attacked.

The protective action of the chlorophyll is the new point which the author considers he has satisfactorily demonstrated. J. W.

**Analyses of Chlorophyll.** By ROGALSKI (*Compt. rend.*, 90, 881—882).—Chlorophyll obtained by Fremieux's method from *Lolium perenne* gave the following results on analysis. The numbers in the second column are the results of an analysis of crystallised chlorophyll made by A. Gautier in 1879:—

|               | Rogalski.          | Gautier. |
|---------------|--------------------|----------|
| C .....       | 73.015             | 73.97    |
| H .....       | 10.377             | 9.80     |
| N .....       | 4.14               | 4.15     |
| O .....       | z                  | 10.33    |
| Ash (Ca)..... | 1.657 (Phosphates) | 1.75     |

C. H. B.

**Alkaloids of Belladonna, Datura, Jusquiame, and Duboisia.** By A. LADENBURG (*Compt. rend.*, 90, 874—876).—*Belladonna*, as is well known, contains atropine and hyoscyamine; *Datura stramonium* contains hyoscyamine, and probably atropine; *jusquiame* contains hyoscyamine and another alkaloid, which gives a compound with gold chloride, fusing at 200°. *Duboisia myoporoides* contains hyoscyamine. Hyoscyamine crystallises in small needles, fusing at 108.5°. It is isomeric with atropine, from which it is distinguished by forming a compound with gold chloride, which fuses at 159°, and has a brilliant lustre, whilst the corresponding atropine compound melts between 135 and 137°, and has no lustre. When treated with baryta, it is easily transformed into tropine and tropic acid, products identical with those obtained from atropine, which, moreover, may be artificially reproduced by heating a mixture of tropine and tropic acid with hydrochloric acid. Hyoscyamine, which comes into commerce as *light atropine*, affects the pupil of the eye in the same way as atropine.

C. H. B.

**Composition of Diastase and Beet Mucilage.** By C. ZULKOWSKI and G. RENNÉ (*Bied. Centr.*, 1879, 929).—Diastase was extracted from malt by glycerol, precipitated and washed with alcohol, redissolved and reprecipitated. A product soluble in water was obtained, having the following composition:—C, 47.57; H, 6.49; N, 3.16; O, 37.64; ash, 3.16 per cent., and a little sulphur.

From beetroot has been extracted by similar means a body containing 5 per cent. of nitrogen, and bearing a great resemblance to Scheibler's "frog spawn."

J. K. C.

**Diastase.** By J. KJELDAHL (*Dingl. polyt. J.*, 235, 379—387, and 452—460).—This research comprises a considerable amount of experimental work undertaken by the author with a view of solving several questions which have arisen as to the active fermenting principle of malt, known as diastase. A normal solution of malt-extract was prepared. As to the influence which diastase is said to exercise on the production of sugar, the author in his investigations arrived at the following law. The proportion of the amount of diastase of two malt-extracts may be expressed by the reducing power which they effect, providing that both act on the same quantity of starch at the same temperature, during the same period of time, and that the reduction does not surpass 25—30. With regard to the influence of temperature on the yield of sugar, a series of trials was made, showing that at temperatures above 63° the fermenting power is weakened, whilst below 63° it does not appear to be affected. It was further proved that by long-continued digestion the same yield can be obtained at all temperatures below 63° as that obtained at 63°, and that the action of diastase at all these temperatures is the same, inasmuch as the yield of sugar may reach the same proportions in each of these cases.

Other questions of minor importance are considered in the original paper, such as the fermenting power of barley, the formation of diastase during the preparation of malt, the diminution of the fermenting power during the baking process, the influence of the concentration on the production of sugar, the influence of foreign ingredients on the yield of sugar, viz., sugar, dilute acids and alkalis, salts of the heavy metals, other salts, alkaloids, alcohol, &c.

In conclusion, the author briefly refers to a substance called ptyalin, the diastase of saliva, which resembles the diastase of malt in several of its properties.

D. B.

**Oxidation of Cholic Acid.** By P. LATSCHINOFF (*Bull. Soc. Chim.* [2], 33, 297).—The formation of stearic and palmitic acids, &c., by the oxidation of cholic acid with potassium permanganate and sulphuric acid (Tappeiner, this Journal, 36, 388), is due to impurities contained in the acid, which are not removed by washing with ether. The acid purified by means of its barium salt does not yield any fatty acids on oxidation.

L. T. O'S.

**Albuminoids.** By W. KNOP (*Bied. Centr.*, 1879, 885—887).—Assuming for albumin the formula  $C_{60}H_{100}N_{16}O_{30}$ , for the purpose of comparison, the author obtains the compounds  $C_{60}H_{97}Br_3N_{16}O_{21}$ ,  $C_{60}H_{98}Br_4N_{16}O_{20}$ , and  $C_{60}H_{98.5}Br_{3.5}N_{16}O_{24}$ , by the action of bromine-water in the cold on albumin. Other brominated products obtained from horn, glue, feathers, &c., differ from albumin by one or more molecules of tyrosine, leucine, and water.

J. K. C.

## Physiological Chemistry.

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**Digestibility and Nutrient Power of Caroba Beans.** By H. WEISKE and others (*Bied. Centr.*, 1880, 110—115).—The experiments were made with two Southdown Merino sheep. The food given consisted of wheat straw, caroba beans, peas, beans, sugar, and starch in various proportions, and the amount of each digested and the influence of the caroba beans on the absorption of the albumin of the other foods observed. In all cases the caroba beans had a depressing influence, so that the albuminoid matter was not so freely digested as when it was absent. Even when large quantities of albuminoid matter were given, such as linseed cake, there was a considerable depression.

E. W. P.

**Quantitative Estimation of Digested Protein.** By O. KELLNER (*Bied. Centr.*, 1880, 107—110).—Schulze has only determined the nitrogen in the biliary secretions which occurs in the fæces of Herbivora fed on food poor in nitrogen. The author has, therefore, undertaken the estimation when the food was poor and rich in nitrogen. The following are a few of his results:—

| Daily food.               | N in biliary secretion. | Digested.   |          | Dry faecal matter. |
|---------------------------|-------------------------|-------------|----------|--------------------|
|                           |                         | Dry matter. | Albumin. |                    |
| Oat straw .....           | 0.257 gr.               | 212 gr.     | 2 gr.    | 319 gr.            |
| Wheat straw.....          | 0.396 „                 | 560 „       | 66 „     | 318 „              |
| Ditto, + 400 gr. beans .. | 0.660 „                 | 651 „       | 141 „    | 315 „              |
| Ditto, + 800 gr. beans .. | 1.007 „                 | 838 „       | 222 „    | 359 „              |

According to the above figures, the nitrogen which is contained in the fæces is very variable, but appears to be directly proportional to the dry matter digested. When food poor in nitrogen is given, the percentage of nitrogen in the fæces appears to increase. It has also been remarked that the outer surface of the fæces of sheep when dry cracks and peels off in thin layers; this outer coating appears to contain a large quantity of mucous matter.

E. W. P.

**Absorption of Various Alimentary Materials in the Human Intestinal Canal.** By M. RUBNER (*Zeits. f. Biologie*, 15, 115—204).—The diet of the persons experimented on was carefully regulated, and the fæces periodically collected and analysed. The difference between the amount of nitrogen, carbohydrates, &c., entering, and that leaving the system in the fæces was thus determined; this difference was regarded as affording a measure of the aliment absorbed in the intestinal canal. The following tables contain the more important numerical results. A lengthy discussion of these results will be found in the original. The quantities of food, &c., are stated in grams.

TABLE I.—*Absorption of Fat.*

| Diet.                                 | Fat in food. | Fat in faeces. | Percentage loss. |
|---------------------------------------|--------------|----------------|------------------|
| Bacon .....                           | 96.0         | 17.2           | 17.4             |
| " .....                               | 191.2        | 15.2           | 7.8              |
| " and butter ....                     | 350.5        | 44.6           | 12.7             |
| Rice and marrow ....                  | 74.1         | 5.3            | 7.1              |
| Eggs .....                            | 118.5        | 5.2            | 4.4              |
| Butter.....                           | 234.3        | 5.8            | 2.7              |
| Potatoes and butter ..                | 143.8        | 5.3            | 3.7              |
| Non-nitrogenous food with butter..... | 157.8        | 2.5            | 1.8              |
| Cabbages and butter..                 | 88.0         | 8.2            | 6.1              |
| Maccaroni with gluten                 | 73.4         | 5.1            | 6.96             |
| " with butter                         | 72.2         | 4.2            | 5.7              |
| Carrots and butter ..                 | 47.0         | 2.5            | 6.4              |
| Maize and butter ....                 | 43.6         | 8.0            | 17.5             |
| Milk .....                            | 160.0        | 7.4            | 4.6              |
| " .....                               | 119.9        | 6.7            | 5.6              |
| " .....                               | 95.1         | 3.0            | 3.3              |
| " .....                               | 79.9         | 5.7            | 7.1              |
| " and cheese ....                     | 213.5        | 24.6           | 11.5             |
| " " ....                              | 138.6        | 3.8            | 2.7              |
| " " ....                              | 133.6        | 10.4           | 7.7              |
| Animal food and butter                | 23.4         | 4.0            | 17.0             |
| " "                                   | 20.7         | 4.4            | 21.1             |

TABLE II.—*Absorption of Carbohydrates.*

| Diet.                              | Carbohydrates in food. | Carbohydrates in faeces. | Percentage loss. |
|------------------------------------|------------------------|--------------------------|------------------|
| White bread .....                  | 670                    | 5                        | 0.8              |
| " " .....                          | 391                    | 6                        | 1.4              |
| Rice .....                         | 493                    | 4                        | 0.9              |
| Maccaroni .....                    | 462                    | 6                        | 1.2              |
| <i>Spritzel</i> <sup>1</sup> ..... | 558                    | 9                        | 1.6              |
| Fat <sup>2</sup> .....             | 259                    | 4                        | 1.6              |
| Diet free from nitrogen            | 674                    | 11                       | 1.7              |
| Maccaroni with gluten              | 418                    | 10                       | 2.3              |
| Maize .....                        | 563                    | 18                       | 3.2              |
| Fat <sup>3</sup> .....             | 226                    | 14                       | 6.2              |
| Fat <sup>4</sup> .....             | 221                    | 14                       | 6.2              |
| Fat <sup>5</sup> .....             | 234                    | 16                       | 6.8              |
| Potatoes .....                     | 718                    | 55                       | 7.6              |
| Black bread .....                  | 659                    | 72                       | 10.9             |
| Cabbages.....                      | 247                    | 38                       | 15.4             |
| Carrots .....                      | 282                    | 50                       | 18.2             |

1. Prepared by mixing meal, water, milk, and eggs to a stiff paste, passing through a wide sieve, and boiling with water.

2 and 3. Fat supplied in form of bacon, eaten alternately with bread and with animal food. 4. Fat supplied in form of butter. 5. In form of butter and bacon.

TABLE III.—*Absorption of Nitrogen.*

| Diet.                 | Nitrogen in food. | Nitrogen in fæces. | Percentage loss. |
|-----------------------|-------------------|--------------------|------------------|
| Animal food .....     | 48·8              | 1·2                | 2·5              |
| " .....               | 40·0              | 1·1                | 2·7              |
| Eggs .....            | 22·8              | 0·6                | 2·6              |
| Milk and cheese.....  | 23·4              | 0·7                | 2·9              |
| " .....               | 24·1              | 0·9                | 3·7              |
| " .....               | 38·9              | 1·9                | 4·9              |
| Milk.....             | 12·9              | 0·9                | 7·0              |
| " .....               | 15·4              | 1·0                | 6·5              |
| " .....               | 19·4              | 1·5                | 7·7              |
| " .....               | 25·8              | 3·1                | 12·0             |
| Leguminous vegetables | —                 | —                  | 10·5             |
| Maccaroni with gluten | 22·7              | 2·5                | 11·2             |
| Maccaroni .....       | 11·2              | 1·9                | 17·1             |
| Cabbages .....        | 13·2              | 2·4                | 18·5             |
| White bread .....     | 13·0              | 2·4                | 18·7             |
| " .....               | 14·7              | 2·3                | 19·2             |
| Maize .....           | 12·0              | 2·3                | 20·5             |
| Spätzel.....          | 8·4               | 2·1                | 25·1             |
| Rice.....             | 7·7               | 1·9                | 25·7             |
| Black bread .....     | 13·3              | 4·3                | 32·0             |
| Potatoes .....        | 11·4              | 3·7                | 39·0             |
| Carrots .....         | 6·5               | 2·5                | 39·0             |

A similar table is given showing the difference between the ash in the food and in the fæces, but the author does not think that the results throw much light on the question of the absorption of mineral matter.

M. M. P. M.

**Interchange of Material in the Animal Organism.** By A. ADAMKIEWICZ (*Bied. Centr.*, 1880, 103—105).—The fact that the animal organism can produce from ammonium salts the more complex constituents of urine has long been known. The author now shows that the quantity of sugar which is produced in urine by diabetic patients, and which is formed by the rapid degeneration of tissue, can be in great part diminished if not altogether caused to cease, by doses of ammonium salts. He considers that the sugar is produced from the albuminous matter, as more sugar is formed than can possibly be formed from the carbon contained in the food. Experiments prove that ammonia when administered does not appear in any form in the urine, and that the sugar also ceases to appear, therefore the conclusion is drawn that the ammonia and the sugar are employed in regenerating the destroyed tissues. After a time, however, the action of the ammonia diminishes; this appears to be due to the presence of a third substance: concerning this point, further investigations are being made.

E. W. P.

**Distribution of Copper in the Animal Kingdom.** By G. BIZIO (*Gazzetta*, 10, 149—157).—This is a claim of priority for his father, B. Bizio, as being one of the first workers in this field, and as



having made most extended investigations. The paper gives a very complete historical survey of the labours of the various chemists who have examined the subject from Sarzeau, who discovered copper in the blood of the bull in 1830, to Giunti whose researches were published in the *Gazzetta* in 1879 (this vol., p. 275). C. E. G.

## Chemistry of Vegetable Physiology and Agriculture.

**Light, Shade, and Soil studied in their Influence on the Growth of Forest Trees.** By M. GURNAND (*Compt. rend.*, 90, 144—146).—The experiments, which lasted during 17 years, were instituted with a view of ascertaining the periodic cubical increase in the wood of a forest of young fir trees extending over an area of 13·3 hectares. The young trees, which were intermingled with leafy copse-wood, were reckoned as forest trees when they measured 0·6 metre in diameter, at a distance of 1·33 metre from the ground.

First period of *six* years: The coppice was from four to ten years old, and covered the ground imperfectly. There were 1,457 trees, the cubical contents of which were 1,424 cubic metres at the beginning, and 2,266 c.m. at the end of the period. The mean yearly increase was 140 c.m. of wood, or 71·5 c.m. of carbon, reckoning 51 per cent. of carbon for every 100 parts of wood.

Second period of *five* years: The coppice was from 11 to 15 years old, and covered the ground completely. Allowing for wood cut down, there were 1,336 firs containing 1,700 c.m., which increased to 2,207 c.m. The mean annual increase was 101·4 c.m. or 51·7 c.m. of carbon, instead of 71·5 c.m. as in the first period, notwithstanding that the actual bulk of wood (1,700 c.m. against 1,424 c.m.) was larger to start with.

Third period of *one* year: During the winter a considerable clearance was made in the underwood, all the oblique or horizontal branches being suppressed, leaving only the vertical branches. The trees numbered 1,057 containing 998 c.m., which at the end of the year measured 1,096 c.m. The increase was 98 c.m. or 50 c.m. of carbon.

In the fourth period of *three* years, with 1,155 trees, the mean annual increase was 87 c.m. or 41·4 c.m. of carbon fixed; and in the fifth period of *two* years, when there were 1,348 trees, the yearly increase was only 47·5 c.m. or 24·2 c.m. of carbon.

The conclusion drawn from these experiments is that the fixation of carbon by the forest tree diminishes in proportion as the shade produced by the underwood becomes more intense, and that this diminution is not prevented by the subsequent suppression of the lateral branches of the coppice. The experiments of Saussure have proved that the carbon or carbonic anhydride required by the plant is not derived from the soil, it is therefore useless to look in that quarter for a solution of the difficulty; it is, on the contrary, much more probable

that a certain increase of carbonic anhydride in the atmosphere is beneficial to the life of the tree, and that this increase of carbonic anhydride results from the decomposition, under the influence of light, of the substances which form humus; if access of light to the soil is prevented by the presence of a leafy undergrowth, the humus-forming substances are not decomposed; carbonic anhydride is not produced, and the trees suffer in consequence, or at least do not flourish to the extent that they would do under opposite conditions.

The author likens humus kept closely in shade to farm-yard manure which has been too deeply ploughed in; both are liable to remain almost inert for several years. J. W.

**Growth of Legumes.** By R. POTT (*Landw. Versuchs.-Stat.*, 25, 57—106).—For the following investigation, 50 sq. m. were sown with horse beans and the same amount with common vetch. Plants were collected at six different periods during their growth from all parts of each field, an average sample being taken. The plants were divided as follows:—The stem cut off close to the crown of the root was divided into three parts, except during the first period. In the first, fifth, and sixth periods the leaves were taken all together; in the other cases the leaves were divided into lower and upper. The flowers were examined separately, also the young pods; and in the last period, the seeds and husks were examined separately.

Numerous tables of results giving the amount of woody fibre, fat, nitrogen-free and nitrogenous compounds, mineral constituents, and nitrogen are given, showing the state of the different parts of the plant at the six periods.

For the horse-bean plant, the author finds that the plant continually increases in weight, most, just before beginning to ripen and least, just about the end of flowering. The formation of woody tissue has its relative and absolute maximum with the ripening of the fruit. Most woody tissue appears in the lower part of the stem. The fatty substances are greatest at the end of the vegetation, but are relatively greatest during flowering time. The absolutely and relatively greatest quantity of nitrogen-free compounds appears before the ripening. The stems are relatively richer in nitrogen-free compounds than the leaves, and these are poorer than the flowers and the pods. The whole plant is richest in nitrogen-compounds during the flowering and is poorest before ripening. The upper parts of the plant are richer in nitrogen than the lower; the least nitrogen relatively is found in the lower part of the stem. With increased age, the leaves become decidedly poorer in nitrogen. Mineral constituents increased during the whole growth of the plant; the absorption was greatest during the flowering period, but the relatively greatest quantity was found during the first period.

In the case of the vetch, the plants were collected at the end of five different periods. Tabular results are given, as in the case of the horse bean, and the author draws the following conclusions:—The plants increase in weight during the whole time. The greatest increase comes just before the ripening is completed, the least at the beginning of ripening. The increase in weight ceases first in the

lower leaves. The absolute maximum of the woody fibre formation occurs at the end of the flowering. The fat is found in greatest quantity after flowering, and is highest in the leaves. The absolutely greatest production of nitrogen-free compounds occurs after flowering, and generally less is found in the leaves than in the stem. Up to the end of flowering, the nitrogen increases, then decreases, again increases, and finally decreases; the maximum occurs when the fruit begins to ripen. The amount of nitrogen per cent. is least at the time when pods cease to grow, whilst it is greatest shortly after the end of flowering. Generally the lower part of the plant is poorer in nitrogen than the upper; the leaves contain more than the stem, and the seeds more than the leaves; but the older the leaves, the less they contain. The ripe plants are richest in ash (per cent.); the maximum absorption compared with the growth takes place at the beginning of ripening.

J. T.

**Formation of Fatty Matter and Ripening of the Olive.** By A. FUNARO (*Gazzetta*, 10, 82—85; also *Landw. Versuchs.-Stat.*, 25, 52—56).—The author made careful analyses of the pulp and kernel of the olive and also of the leaves of the plant at intervals between the 25th of July and 25th of February, the results of which are given in three tables. The author finds, with De Luca and Roussille, that the formation of the kernel precedes that of the pulp, and that as the weight of the olive and of the fatty matter it contains increases, the water slowly diminishes. Mannitol is found in small quantity in the fruit, but cannot be detected in the leaves until the greater part of the fatty matter has been formed in the fruit. From this it is inferred that the presence of mannitol has no relation to the formation of the fatty matter, but rather that it is a product of the metamorphoses of the carbohydrates. Its presence in the olive is accounted for when we consider that it belongs to the same family of plants as the ash.

C. E. G.

**Amount of Albuminoids in Potatoes.** By F. HOLDEFLEISS (*Biol. Centr.*, 1880, 120—122).—Analyses of 19 different sorts of potatoes show that the amount of albuminoids (calculated by  $N \times 6.25$ ) is not dependent on the sp. gr. nor on the starch; the quantity varies from 6—11 per cent. of the dry matter, the mean being  $2.3\frac{1}{2}$  per cent. of the original material.

E. W. P.

**Existence of Ammonia in Vegetables.** By H. PELET (*Compt. rend.*, 90, 876—879).—The leaves of the beetroot contain 0.0138, the root 0.029, and the seeds 0.192 per cent. of ammonia. Phosphoric acid is in each case present in the proportion required to form magnesium ammonium phosphate, whilst the magnesia is in slight excess. Wheat contains 0.16 per cent. of ammonia and 0.74 per cent. of phosphoric acid. The whole of the magnesium is probably in the form of magnesium ammonium phosphate, whilst the excess of ammonia exists as double salts of ammonium and potassium.

C. H. B.

**Lime in Plant-Life.** By E. v. RAUMER and C. KELLERMANN (*Landw. Versuchs.-Stat.*, 25, 25—38).—Stohmann has shown (*Annalen*, 121) the necessity of lime for the development of plants, but its func-

tion has not been fully made out. Bohm has shown that lime is necessary, in the earliest stages of plant life, for the consumption of the non-nitrogenous reserve stuff; he also concluded that lime was as necessary to the building up of plant structure as to the change of cartilage into bone. From the rapid absorption of lime by sprouting bulbs, and the simultaneous appearance of calcium oxalate, Kellermann supposed that lime might act on the solution of the starch by the formation of a ferment. The experiments on bean plants detailed in the paper were conducted by Raumer. Some of the plants were grown in acid-washed quartz-sand and fed with different solutions, both free from and containing calcium salt; others were grown in water and solutions with or without calcium salt; the plants produced were examined microscopically only. The results agree essentially with those of Bohm and others, and show specially that the function of the lime is closely connected with the consumption of carbohydrate; further, the amount of lime present in the seed is not sufficient for the use of the non-nitrogenous reserve stuff. Whether the lime acts in the dissolving and transport of the reserve starch, or in the decomposition of the starch to form cellulose, is a difficult question to answer, but the weight of evidence is in favour of the latter view. The investigation is to be continued.

J. T.

**Relation between the Sugar and Mineral and Nitrogenous Matters in Normal Beetroot and in Beetroot Run to Seed.** By H. PELLET (*Compt. rend.*, 90, 824—827).—The author considers that a constant relation exists between the amounts of sugar and phosphoric acid (100 to 1.15), and that the latter is the most important constituent in the manures to be applied. The amounts of lime and magnesia in the plant vary but slightly, but the potash and soda are liable to much greater variations, replacing each other in equivalent proportions, so that the amount of sulphuric acid necessary to combine with the mineral matter in the ash remains almost the same. Next to phosphoric acid, magnesia and lime are the most important constituents of the manures employed, then come potash and soda, and lastly nitrogen. The richer the beetroot is in sugar, the less mineral matter does it contain, but the quantity of leaves is greater and they leave more ash. If, however, the leaves are left on the soil, proportionally more mineral matter is restored to it. In other words, the higher the yield of sugar, the less is the soil impoverished. The German roots contain less chlorine and much less nitrogen than those grown in France, but are richer in sulphuric acid. The Siberian roots contain much more soda than is found in the French roots. The phosphoric acid probably exists in the root in the form of ammonium magnesium phosphate, since the acid and the magnesia are always present in the proportions in which they exist in this compound.

C. H. B.

**Manuring of Field Beans.** By L. RIDOLFI (*Bied. Centr.*, 1880, 153).—Field beans were grown on four plots manured as follows:—I, unmanured; II, 100 kilos. nitrogen as ammonia salts; III, 65 kilos. nitrogen as ammonia, and 50 kilos. phosphoric acid as super-

phosphate; IV, 200 kilos. phosphoric acid as superphosphate. The results per ha were as follows:—

| Plot,    | Beans.  |        | Straw. |                             |
|----------|---------|--------|--------|-----------------------------|
|          | Litres. | Kilos. | Kilos. | Weight of hectol. in kilos. |
| I.....   | 2,000   | 1,575  | 2,000  | 78·75                       |
| II.....  | 2,540   | 1,524  | 2,244  | 80·00                       |
| III..... | 3,060   | 5,204  | 2,700  | 71·99                       |
| IV.....  | 3,200   | 2,860  | 2,757  | 89·37                       |

The percentage composition of the beans did not greatly vary; plot II gave a maximum 5·26, and I only 4·275 of nitrogen, while III gave maximum of ash 3·8.

In 100 parts ash was found:—

*Beans.*

|  | I.    | II.   | III.  | IV.   |
|--|-------|-------|-------|-------|
| P <sub>2</sub> O <sub>5</sub> .....      | 45·5  | 27·48 | 4·3   | 41·4  |
| SO <sub>3</sub> .....                    | 6·46  | 8·23  | 6·1   | 5·6   |
| Cl.....                                  | 1·3   | 3·3   | 4·3   | 1·64  |
| Na <sub>2</sub> O, K <sub>2</sub> O..... | 32·61 | 45·79 | 33·83 | 38·97 |
| CaO.....                                 | 5·59  | 6·59  | 5·6   | 5·75  |

*Straw.*

|  | I.    | II.   | III.  | IV.   |
|--|-------|-------|-------|-------|
| P <sub>2</sub> O <sub>5</sub> .....      | 5·15  | 3·92  | 4·00  | 3·2   |
| SO <sub>3</sub> .....                    | 8·57  | 5·05  | 5·05  | 0·16  |
| Cl.....                                  | 0·91  | 1·78  | 1·73  | 0·14  |
| Na <sub>2</sub> O, K <sub>2</sub> O..... | 49·34 | 51·25 | 45·87 | 36·43 |
| CaO.....                                 | 30·25 | 32·70 | 33·21 | 18·33 |

E. W. P.

**Experiments with Manures.** By M. LECLERC and M. MOREAU (*Bied. Centr.*, 1880, 100—103).—The following were employed as manures through a six years' course of potatoes, oats, flax, cole-rape, beans with vetches, oats: (1) stable manure; (2) artificial manures; (3) stable and artificial manures mixed. These were sown with the seed on plots of 7½ ars, and a similar plot was left unmanured for comparison. The yield of the various crops, with their money value, and also that of the manures, are carefully enumerated.

In each year, a slight change in the quantities of the manure was made, but the materials employed were the same. A second series of

experiments is also detailed; in this series, the crops were grown upon land which was less rich in organic matter, and the course consisted of potatoes, wheat, clover, oats, potatoes and oats; in neither case is any inference drawn from the experiments. E. W. P.

*Note by Abstractor.*—In many cases it appears, according to the figures in the above paper, that the expense of the manure more than counterbalanced the gain of the manured over the unmanured crop; as for example, value of unmanured crop of oats was 358 marks, that of the crop manured with ammonium sulphate was 430 marks, whereas the value of the manure was 164 marks.—E. W. P.

**Reduction of Superphosphates, and the Behaviour of Phosphoric Acid in Soils.** By H. JOULIE, H. ALBERT, and H. VOLLBRECHT (*Bied. Centr.*, 1880, 81—87).—Joulie states that all aluminium phosphates are soluble in ammonium citrate, but that the iron phosphates are less soluble, the more basic they be; they dissolve, however, if treated with ammonium citrate and sulphide. In a mixture of mono- and di-calcium phosphates with aluminium and ferric hydrates, the greater part of the phosphates are no longer soluble in water and citrate, which proves the combination of part of the phosphoric acid with the last-named oxides; hence tricalcium phosphate must be formed. Tricalcium phosphate is also less soluble in ammonium citrate, the drier it is. It is further shown that if superphosphate be prepared with the requisite quantity of sulphuric acid, a moist product is the result when the phosphate contains large quantities of iron and calcium compounds. If a dry compound is produced, and this occurs when there is an insufficiency of acid, the superphosphate is rapidly reduced to the tribasic salt. The same occurs, if calcium carbonate be added.

Albert and Vollbrecht show that in a calcareous soil the reduction takes place most rapidly under the influence of light, and that the dicalcium salt also becomes tricalcium phosphate in the soil.

All the phosphates, including ferric and aluminium, whether originally insoluble or only partly so, become soluble in very peaty soils, the cause being in all probability the action of the humic acid. It is therefore most economical for the manuring of peaty soils to use only one-third of the sulphuric acid generally employed when preparing soluble phosphate, so that dicalcium phosphate only may be produced. Hence, composts of turf, or stable manure with insoluble phosphates, are valuable. E. W. P.

**Agricultural Value of Reduced and Insoluble Phosphates.** By A. PETERMANN and others (*Bied. Centr.*, 1880, 87—99).—Petermann's experiments were made with (1) superphosphate containing about 15 per cent. of soluble phosphoric acid; (2) superphosphate containing 7 per cent. of phosphoric acid soluble in water, and 2 per cent. soluble in ammonium citrate; (3) precipitated phosphate containing about 20 per cent. of the acid soluble in citrate; (4) ignited precipitated phosphate containing about 3 per cent. soluble in citrate; the crops were peas and barley. He comes to the conclusion that in

many cases the "reduced" phosphate is of greater value than the superphosphate. In sandy soils the soluble phosphate is washed away from the roots; if the superphosphate does not show marked action, on limey soils, it is due to the formation of tricalcium salt, while the "reduced" on the same soil remains unaltered. On sandy soils having a small percentage of lime, the "reduced" often shows a better result than the "soluble." This is probably due to the production of ferric and aluminium phosphate. The results with ignited phosphates are unsatisfactory.

De Leeuw finds that on a soil containing no lime and much humus, the insoluble phosphates are the most satisfactory. Fleischer states that when the same sort of manures as above are applied to a peaty soil, the difficultly soluble phosphate is of more value than on other soils. E. Wein has employed the same manures, with the addition of Chili saltpetre to "soluble" and "reduced" phosphates, on a sandy lime soil, and finds that the yield of grain (rye being the crop) is increased by the addition of phosphates, and the yield of straw trebled on those plots to which the nitrate had been added. The nitrate and reduced phosphate yielded the best crop. Phosphates increase the amount of dry matter; for cereals, on the above class of soils, phosphorite phosphate is better than guano superphosphate; bibasic phosphate is best for peas; aluminium and ferric phosphates produce a better crop than if no phosphates had been added; tricalcium phosphate gives no results. With oats, the results are similar. On light, calcareous soils reduced phosphate is better than soluble phosphate for all crops.

E. W. P.

**Sulphurous Acid as a Remedy for Bunt in Wheat.** By A. ZOEBL (*Bied. Centr.*, 1880, 129—133).—The spores of bunt or "stinking smut" (*tilletia caries*) are readily destroyed by fumigation with sulphurous anhydride. It is recommended to burn sulphur in a large cask, which is then half or three-quarters filled with the grain, and subsequently rolled. The spores are destroyed in a few minutes, whereas the vitality of the wheat remains for the most part unimpaired even if exposed to the gas for 3—4 hours.

E. W. P.

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## Analytical Chemistry.

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**Determination of Specific Gravity.** By A. W. BLYTH (*Analyst*, 1880, 76).—The sp. gr. of solid butter fat may be determined at 15° with great accuracy as follows:—A short wide test-tube is weighted with lead or mercury and weighed in water, the height of the water in the beaker being noted and kept constant in future determinations.

The tube is now filled with a weighed quantity of butter fat and weighed again in water. The sp. gr. of other organic solids may be determined by this method. A section of the solid is cut with a cork

borer, so that it tightly fits the weighed test-tube containing mercury, and is covered by the latter. It is then weighed in water as above.

If the solid is porous, the tube containing the solid is fitted with a doubly perforated cork, in which is inserted a stoppered funnel containing mercury, and a glass tube connected with a Sprengel pump; the air is exhausted, and a stream of mercury allowed to pour in, the pores are thus completely filled with mercury. L. T. O'S.

**Filter-paper and Filtering.** By K. KRAUT (*Zeits. Anal. Chem.*, 1879, 543—546).—Independently of mechanical means for hastening filtration, the author finds that attention to the quality of the paper used and to the shape of the funnel employed, will produce very considerable increase in the rapidity of filtration. The angle of the funnel must be a right angle, and the paper fit it evenly without interposed air-bubbles; but further, the tube of the funnel must be of the right diameter and uniform throughout, any enlargement or constriction retarding the passage of liquid: in one series of experiments the time of filtration was increased fourfold by the use of a badly shaped funnel. The paper should be uniform in quality, and should not swell too rapidly when wetted; it should also readily allow the passage of liquid whilst retaining fine particles of precipitate. The quality of the paper used, and the length of time it had been wetted, produced very great variations in the rapidity of transmission of the liquid. The best paper experimented on by the author was of Danish make.

F. C.

**Estimation of Carbonic Anhydride in Gases.** By A. GAWALOVSKI (*Zeits. Anal. Chem.*, 1879, 560—563).—An apparatus is described for determining the proportion of carbonic anhydride present in the gas used for "saturation" in sugar refining, or for making mineral water or for other purposes, where the carbonic anhydride is mixed with other gases not absorbed by caustic alkali. Its claims over other existing forms of apparatus are that it is less fragile, it dispenses with stopcocks, is of smaller dimensions, and is cheaper; at the same time it is sufficiently accurate for commercial purposes.

The apparatus consists of an upright graduated measuring tube closed above, into the lower end of which a U-shaped funnel tube can be fitted, the whole forming a U-tube. Two measuring tubes are provided each of 200 c.c. capacity, the one broad above and narrow below, the other narrow above and expanded below, the enlarged part being divided by 50 c.c. graduations and the narrow part into  $\frac{1}{4}$  c.c. One or other of these tubes is used according as the proportion of carbonic anhydride present is large or small. The measuring tube is filled with the gas over salt-solution up to the 200 c.c. mark, then removed into a vessel containing caustic soda solution, and after the soda solution ceases to rise by further agitation, showing the absorption to be complete, the funnel tube is connected under the solution; the temperature of the gas is then lowered by immersion of the apparatus in a vessel of cold water, the levels of liquid in measuring tube and funnel tube are equalised, and the volume of unabsorbed gases is read off. To avoid error by capillarity, the tubes must be of the same diameter at the upper surfaces of the liquid. F. C.



**Reduction of Carbonic Anhydride to Carbonic Oxide by Red-hot Stannous Oxide.** By A. WAGNER (*Zeits. Anal. Chem.*, 1879, 559—560).—In the course of experiments made to ascertain whether stannous oxide could be substituted for chromic oxide in the author's process for estimating nitrates, it was noticed that carbonic anhydride was reduced to carbonic oxide by the heated stannous oxide. The author describes in the present paper experiments which fully confirm this result. Hence the method of dehydrating stannous hydrate by heating it in a stream of carbonic anhydride is unsatisfactory, since it furnishes stannous oxide more or less mixed with stannic oxide.

Similar experiments proved that carbonic anhydride is reduced in an analogous manner by red-hot ferrous oxide. F. C.

**Formation of Nitric Oxide by Ignition of Nitre.** By A. WAGNER (*Zeits. Anal. Chem.*, 1879, 552—558).—The method already described by the author (*ibid.*, 11, 91) for estimating nitric acid by igniting a nitrate with excess of chromic oxide and alkaline carbonate in a stream of carbonic anhydride, is found to give accurate results either by estimating the chromate formed or the nitric oxide evolved. In the case of other gases being evolved, the author suggests oxidising the nitric oxide by oxygen gas over standard alkali solution, and titrating the excess of alkali: and he suggests adapting the process to the estimation of nitric acid in drinking-water by oxidising the organic matter by potassium permanganate first in alkaline then in acid solution.

A direct experiment in which the nitre was estimated by reading off the volume of nitric oxide liberated, gave 0.7 per cent. excess of nitre.

A series of trials with other oxidisable oxides in place of the chromic oxide, proved that with all other oxides a deficiency of nitric oxide was obtained; cuprous oxide yielded 3 per cent. deficiency, manganoso-manganic oxide 4 per cent., and manganous carbonate about 15 per cent. F. C.

**Contribution to the Knowledge of "Reduced" Phosphoric Acid.** By C. F. MEYER (*Zeits. Anal. Chem.*, 1880, 145—150).—

1. *Process of Reduction.*—Wagner explains the so-called "reduction" of phosphoric acid in ferriferous and aluminiferous superphosphates by the conversion of ferric and aluminic sulphates, in the presence of monobasic calcium phosphate, into acid ferric and aluminic phosphates with separation of gypsum. The two last-named phosphates considerably influence the quality of the superphosphate, as they occasion the formation of an insoluble precipitate.

In investigating this point, the author found that the concentration of the solution containing the calcium phosphate materially retards the formation of this precipitate. He explains the "reduction" of the phosphoric acid by the simultaneous action of tribasic calcium phosphate, monobasic calcium phosphate and ferric sulphate on one another, and proves by a series of chemical equations that this action is facilitated by the presence of ferric and aluminic sulphates in ferriferous and aluminiferous superphosphates.

2. *Separation of Ortho- and Pyro-phosphoric Acids.*—In these ex-

periments dibasic calcium phosphate was used. 5 grams of the phosphate were ignited until constant in weight. The resulting calcium pyrophosphate was decomposed with sulphuric acid, and the lime separated with alcohol. The solution was diluted to 200 c.c.

1. 10 c.c. neutralised with ammonia gave, when heated with ammonium (or sodium) acetate and uranium nitrate, a perfectly clear solution. On cooling, the salt was partly separated.

2. 10 c.c. diluted to 120 c.c. with water and treated with ammonium chloride, magnesia mixture, and ammonia, did not give a precipitate. 1 gram of the above phosphate was ignited, dissolved in hydrochloric acid, neutralised with ammonia, and the solution made up to 200 c.c.

1. By heating the solution with ammonium acetate, the calcium pyrophosphate was separated almost entirely, so that ammonia produced only a slight turbidity in the filtrate.

2. 50 c.c. treated with ammonium citrate and chloride did not give a precipitate with magnesia mixture and ammonia.

3. By heating the resulting precipitate with ammonium acetate and uranium nitrate, it could only be dissolved with great difficulty. It was impossible to obtain a complete solution with sodium acetate.

Fresenius states that ammonium molybdate with the addition of nitric acid does not precipitate pyrophosphoric acid; the author, however, constantly obtained a yellow precipitate.

In conclusion, he says that he has not yet been able to ascertain how far these methods are capable of being applied for the quantitative separation of ortho- and pyro-phosphoric acids. Further trials are being made.

D. B.

**Volumetric Determination of Phosphoric Acid by Means of Uranium in the presence of Iron.** By C. MOHR (*Zeits. Anal. Chem.*, 1880, 150—153).—2 or 5 grams of the finely-powdered mineral are boiled repeatedly with small quantities of dilute nitric acid, and the solution is made up to 250 c.c. When soluble phosphoric acid is determined in superphosphates, the same proportion is used, except that distilled water is employed instead of nitric acid. 10 or 25 c.c. of the filtered solution are treated with a solution of sodium acetate until the turbidity first formed no longer disappears. The solution of acetate of uranium is then added, and the mixture heated gradually to the boiling point. Before the end of the total precipitation has been reached, a few granules of potassium ferrocyanide are added. The ferric phosphate is thus decomposed, the phosphoric acid goes into solution, the ferric oxide forms Prussian blue, and becomes mixed with the uranium phosphate. It is essential not to proceed with the precipitation of the phosphoric acid until all the iron has been precipitated, which is easily recognised by treating a drop of the supernatant liquid with potassium ferrocyanide on a porcelain plate.

In this way determinations of phosphoric acid may be made with a standard solution of uranium in cases where its use was hitherto not practicable, and although this process cannot compete with the molybdic acid method, its application may be recommended especially for laboratories in connection with sewage and manure works on account of its simplicity and rapidity.

D. B.

**Analysis of Mineral Superphosphates and of "Phosphate Précipité."** By BRUNNER (*Zeits. Anal. Chem.*, 1880, 141—145).—The methods described by Fresenius, Neubauer, and Luck, for determining the "assimilable" phosphoric acid in superphosphates (*ibid.*, 10, 133) appear to have been surpassed by the improvement recently made by Petermann, who succeeded in removing several weak points, inherent in the above methods. The object of the present paper is to describe this improved method, which was accepted as a commercial test by the Belgian Government in February of last year. A certain percentage of "acide phosphorique anhydride assimilable" is guaranteed. This includes the total phosphoric acid in the compounds soluble in water and in ammonium citrate.

The solution of ammonium citrate is prepared by dissolving citric acid in ammonia, and making it up to a density of 1.09, taking care that the solution has a distinctly alkaline reaction. It is then filtered and kept in a well-stoppered bottle: 100 c.c. of this solution are brought into a small wash-bottle. A weighed quantity of the manure to be analysed is then washed into a small porcelain mortar, ground up with the pestle, and the mixture transferred to a flask, using the remaining citrate solution to wash out the mortar. After warming the flask for one hour at 35° C. exactly, and repeatedly agitating it, the mixture is made up to 500 c.c. and filtered. The first portion of the filtrate is rejected, as the mixture never filters clear in the commencement; 50 or 100 c.c. of the clear filtrate are then precipitated with a sufficient quantity of magnesium chloride rendered strongly alkaline, and filtered after six hours' standing. The ammonia is removed by washing, and the precipitate ignited and weighed in the usual manner, as magnesium pyrophosphate.

D. B.

**Volumetric Estimation of Sulphates.** By H. PRECHT (*Zeits. Anal. Chem.*, 1879, 521—523).—Normal barium chloride solution is added until the sulphate is exactly precipitated, the final reaction being evident in a clear solution: if the liquid is not clear, the standard solution is added in excess, and the excess is estimated by adding standard potassium chromate solution in quantity more than sufficient to precipitate as chromate the barium present in solution, and then titrating the excess of chromate by standard ferrous sulphate. The potassium chromate is made of half the strength of the barium chloride; 10 c.c. of it are added to the precipitated solution, and the liquid is neutralised by addition of sodium hydrate, an excess of which is harmless. If the yellow colour of the solution is not permanent, 10 c.c. more of the chromate are added, and the addition continued, if necessary, until the yellow colour remains. The liquid is made up to half a litre, and 50 c.c. are filtered off, acidified with dilute sulphuric acid, and titrated with iron solution of one-tenth the strength of the chromate; the end of the reaction is seen by the change of colour from yellow to green, and is exactly found by adding a drop of it to potassium ferricyanide on a white porcelain surface. 10 c.c.  $\text{FeO}$ , divided by 2, gives the excess of barium chloride added, and each cubic centimetre of the latter indicates 40 mgrms.  $\text{SO}_3$ . The method is very

exact, and is applicable in the absence of substances, which would reduce the chromate or oxidise the ferrous solution. F. C.

**Estimation of Potassium as Platinochloride.** By H. PRECHT (*Zeits. Anal. Chem.*, 1879, 509—521).—This method of determining potassium seems to be the only one in general use, all others having proved to be less trustworthy. The author gives an account of a careful examination into the sources of error, and into the best mode of conducting the analytical processes.

1. *Preparation of the Platinic Chloride.*—If the alcoholic washings are evaporated to recover the platinum they contain, it is impossible to precipitate all the platinum with potassium or ammonium chloride, since the compound  $C_2H_4PtCl_6$  is formed, and is not thus precipitable; an explosive compound is also liable to separate. The evaporated washings are best reduced by mixing them with sodium carbonate solution, glycerol, formic acid, or grape-sugar, and boiling. Potassium platinochloride if present is gradually reduced if shaken up occasionally with the liquid, but it is more rapidly reduced by being boiled with caustic soda solution of 1·2 sp. gr., containing 8 per cent. of glycerol. The reduced platinum-black is washed with hydrochloric acid and water until it is free from sulphuric acid and potassium salts; it must never be reduced by potassium instead of sodium carbonate or hydrate, or a large quantity of potassium is retained. Platinum reduced from alcoholic solution contains some of the above explosive compound, and glows when dried on the water-bath; it is only quite freed from this body by heating to redness, and this is necessary to remove any carbonaceous substances which would hinder the solution in acids. If reduced by soda and glycerol, the platinum appears to be pure, and is easily soluble in aqua regia. After dissolving the platinum by hydrochloric and nitric acid in the usual way, the excess of nitric acid is removed by alternate evaporation with hydrochloric acid and water; its removal is necessary because it leads to formation of  $2HNOCl.PtCl_4$ , and promotes the crystallisation of the platinic chloride. The above double chloride forms a yellowish-brown deposit of cubic crystals; it is very deliquescent and soluble, and is decomposed by water, yielding ultimately  $2HCl.PtCl_4$ , nitric acid, and nitric oxide; so that the evolution of nitric oxide on diluting the solution with water is a proof of the presence of this double chloride. A platinic chloride solution should be as free as possible from nitric acid, hydrochloric acid, and platinous chloride; the presence of platinous chloride yields too high results, since it separates on addition of alkaline chlorides; the presence of nitric acid to the extent of 4 per cent. of strong acid was found to make the results 0·05 to 0·1 per cent. too low by increasing the solubility of the platinochloride. The presence of platinous chloride is more detrimental than that of nitric acid. Although ignited iridium is not soluble in aqua regia, it is soluble if alloyed with platinum; it may be separated from the solution by Gibb's method, but its removal is scarcely necessary, since potassium chloride precipitates platinum from the solution before iridium; and even if iridium should partially replace platinum in the precipitate, the atomic weights of the two metals are sufficiently close to prevent any

considerable error arising. The platinum chloride used for estimating potassium should dissolve entirely in alcohol, and give the theoretical quantity of potassium platinochloride when precipitated with pure potassium chloride. A table is given showing the percentage of platinic chloride contained in a solution of known sp. gr.; the determinations required for this table were made with solutions containing 2.24 parts of free hydrochloric acid to every 100 of platinic chloride: the solutions were evaporated and the residue ignited in hydrogen.

2. *Solubility in Alcohol of the Platinochlorides of the Alkali and Alkaline Earth Metals.*—The solubility of *potassium platinochloride*, as determined by Fresenius, is such as to render necessary a correction for what is dissolved by the alcohol used in washing; the author determined the solubility of the pure salt with every precaution, and found it to be much less than Fresenius stated, 1 part of the salt dissolving in 42,600 parts of absolute alcohol, or in 37,300 parts of alcohol of 96 per cent. by weight, or in 26,400 parts of alcohol of 80 per cent. by weight.

*Sodium platinochloride* crystals contain 6 mols.  $H_2O$ , and are triclinic prisms or tables. The dried salt when dissolved in hot alcohol crystallises free from excess of sodium chloride. This salt dissolves to almost any extent in boiling water; the aqueous solution saturated at  $15^{\circ} C.$  contains 39.77 per cent. of anhydrous salt: addition of alcohol causes separation of the salt in a crystalline condition. A saturated solution in 50 per cent. alcohol contains 17.85 per cent. of salt. The water of crystallisation is almost entirely expelled at a temperature below  $100^{\circ}$ ; the anhydrous salt dissolves much more copiously in alcohol than the crystalline, and with evolution of heat. The salt perfectly freed from water by drying at  $150^{\circ}$  dissolved in absolute alcohol to the extent of 48.3 per cent.; after being dried on the water-bath 32.8 per cent. was dissolved; on addition of a few drops of water, these solutions solidify to a mass of the hydrated crystalline salt. As the temperature rises the solubility of the salt is much increased; addition of ether to the alcohol solution causes separation of the salt, and in a mixture of alcohol and ether in equal proportions, only 2.43 per cent. remains dissolved. The salt is insoluble in ether free from alcohol; it is unchanged by boiling with alcohol, but if ether is present, it is partially decomposed into sodium chloride and a combustible compound of hydrogen and platinum chloride.

*Magnesium platinochloride* was prepared by mixing the two chlorides in molecular proportions; it crystallises with  $6H_2O$ ; it dissolves in absolute alcohol to the extent of 43.2 per cent., and when dried at  $150^{\circ}$  is less soluble, only 37.8 per cent. entering into solution.

*Barium platinochloride* can only be obtained from a solution which contains excess of barium chloride; the crystals contain  $H_2O$ ; they are partially decomposed by water and entirely by boiling alcohol into the two chlorides. The presence of four times the theoretical proportion of platinum chloride was found insufficient to convert barium chloride into the platinochloride soluble in alcohol. The anhydrous salt yielded 94.8 (?) per cent. of insoluble barium chloride when washed with absolute alcohol.

*Strontium platinochloride* is a salt soluble in water, and decomposed to a less extent by absolute alcohol than the barium salt. The crystals after being well washed with alcohol left 4·2 per cent. of insoluble strontium chloride.

*Calcium platinochloride* crystallises with  $8\text{H}_2\text{O}$ , is deliquescent in the air; its alcoholic solution contains 53 per cent.

3. *Operations in estimating Potassium.*—When potassium is to be separated from sodium and magnesium salts and weighed as platinochloride, the metals must be present as chlorides: sulphates are best removed by addition of barium chloride solution of known strength to the boiling liquid, which contains 0·5 of hydrochloric acid to every one part of salt. The precipitation is carried out in a half-litre flask, which is cooled and filled to the mark as soon as neither barium chloride nor sulphuric acid causes any precipitate, a further quantity of water is added equal in volume to the barium sulphate precipitate, whose sp. gr. is 4·2. The use of standard barium chloride solution serves to determine the amount of sulphates present during their separation; its strength is 104 grams of anhydrous salt in a litre. The coprecipitation of potassium salts leads to a very slight minus error, amounting to 0·045 per cent. of potassium chloride in kieserite containing 12—14 per cent.

Finkener's method is to be recommended when sulphates or sodium salts are present in large proportion, since it economises platinum chloride solution and alcohol. According to this method, sufficient platinum chloride is added to entirely precipitate the potassium, the precipitate is washed with alcohol, reduced, and the well washed platinum weighed. It requires little more time than the process already described with preliminary precipitation of the sulphates.

The presence of magnesium chloride does not occasion error in the estimation of potassium, since magnesium platinochloride is much more soluble in alcohol than the sodium salt. But as barium platinochloride is decomposed by alcohol, yielding insoluble barium chloride, the presence of barium always leads to high results. It may be stated generally that the presence of barium chloride or of sulphuric acid is inadmissible in estimating potassium.

In working with pure potassium salts, 15·2805 grams are dissolved in a half litre, and 10 c.c. of the solution are taken, each milligram of the platinochloride then corresponds to 0·1 per cent. of potassium chloride; if the potassium is returned as sulphate, 17·847 grams are dissolved. Larger quantities are necessary for determining potassium with accuracy in carnallite, 20 grams being dissolved in 500 c.c., and 25 c.c. of this solution being employed. After adding platinum chloride, the solution is evaporated until it crystallises on cooling, the formation of large crystals being avoided; if sodium platinochloride alone has to be separated, it is best to evaporate quite to dryness, since the sodium salt is more soluble when anhydrous, the use of hot alcohol renders the washing more rapid for the same reason. The use of a mixture of alcohol and ether is to be avoided, since the sodium salt is only dissolved by it with difficulty.

The precipitate may be weighed on a filter previously dried for two hours at  $130^\circ\text{C}$ .; if washed with absolute alcohol, it is perfectly dried

by heating for 20 minutes at 130° C. The use of glycerol is not recommended.

Small quantities of potassium chloride in presence of much sodium chloride are best estimated by adding sodium platinochloride solution to the solution of from 10—100 grams of the salts, and evaporating: the precipitate is washed with absolute alcohol, and the platinum contained in the sodium platinochloride present in the washing is separated, washed, and weighed. This is the only method which gives correct results when less than 2 per cent. of potassium chloride is present. F. C.

**Direct Determination of Soda in Potashes.** By A. v. HASSELT (*Zeits. Anal. Chem.*, 1880, 156—159).—It is known that sodium chloride is but sparingly soluble in concentrated hydrochloric acid; this applies also to potassium chloride, which nevertheless is much more readily soluble than the sodium salt, as illustrated by the following table:—

10 c.c. of the saturated solution of sodium chloride in hydrochloric acid of 1·189 sp. gr. contain when prepared—

|               |                  |
|---------------|------------------|
| at 13·6°..... | 0·0091 gram NaCl |
| 15·2°.....    | 0·0092 „ „       |
| 25·0°.....    | 0·0114 „ „       |

10 c.c. of a similar solution of potassium chloride contain—

|             |                 |
|-------------|-----------------|
| at 15°..... | 0·1280 gram KCl |
| 15·5°.....  | 0·1284 „ „      |

A hydrochloric solution of potassium chloride, saturated at a temperature of 15·3°, was treated with solid sodium chloride, and 10 c.c. evaporated to dryness. The residue amounted to 0·1380 gram “salt-mixture.” This shows that the solubility of sodium chloride is not increased by the amount of potassium chloride present in the solution; the solubility, moreover, of sodium chloride in hydrochloric acid of the above strength is not appreciably increased by raising the temperature of the solution.

From these results, the author inferred that 100 c.c. of hydrochloric acid of the above strength, previously saturated with sodium chloride, would dissolve the quantity of potassium chloride obtainable from 1 gram of potash, whilst the sodium chloride formed from the soda present would remain undissolved. The sodium chloride is allowed to settle, and after removal of the bulk of the acid solution is collected on a vacuum filter, washed with some of the hydrochloric acid solution of sodium chloride, dried at 150°, and weighed. A simple and ingenious apparatus, which greatly facilitates this operation, is described in the paper. As to the other impurities present in potash, it is mentioned that they can be removed by treating the potash with water and filtering the solution. Silicic acid if present could be removed by evaporation in the usual manner. D. B.

**Removal of Large Quantities of Sodium Chloride in Mineral Analyses.** By F. MUCK (*Zeits. Anal. Chem.*, 1880, 140).—In

fusing with alkaline carbonates, neutralising the free acid with sodium carbonate, precipitating iron and alumina with sodium acetate, &c., the resulting solutions often contain as much as 40, 50, and 60 grams of sodium (and potassium) chloride. Under such conditions an accurate determination of magnesia, which requires all possible concentration, cannot be carried out successfully. The author removes the alkaline chlorides as follows:—The filtrate containing the magnesia is evaporated to dryness, treated with cold fuming hydrochloric acid, and the mixture allowed to stand for a few minutes, having previously well stirred it. The whole is then filtered through a filter formed of alternate layers of coarse glass and cotton, and finally washed on the filter with fuming hydrochloric acid. The residue from the evaporated filtrate contains, besides magnesium chloride, only very small quantities of fixed chlorides, and requires but little water to dissolve it.

D. B.

**Action of Fused Alkaline Carbonates on Platinum.** By L. KONINCK (*Zeits. Anal. Chem.*, 1879, 569).—Fusion of 6 grams of  $\text{KNaCO}_3$  in a platinum crucible over a Bunsen flame and blowpipe flame, removed 1 mgrm. of platinum. The presence of manganese raised this loss to 1.5 mgrm. and 1.7 mgrm. in two other fusions, probably owing to the formation of alkaline manganate. By keeping 23 grams of  $\text{KNaCO}_3$  in fusion for fifteen minutes at a high temperature by means of the blowpipe, 3.8 mgrms. of platinum were rendered soluble in water, and in this case, as in those cited above, this weight of platinum was found in the solution of the fused mass. Hence when a substance is decomposed by fusion with alkaline carbonates in a platinum crucible, it is necessary to allow for platinum entering into solution and to precipitate it with sulphuretted hydrogen in the copper and arsenic group.

F. C.

**Lithium Phosphates.** By G. MERLING (*Zeits. Anal. Chem.*, 1879, 563—568).—The accuracy of the method of estimating lithium as orthophosphate having been called into question, the author has confirmed its trustworthiness by preparing pure lithium carbonate from lepidolite, and precipitating a known quantity as phosphate: after observing all due precautions detailed below, 104.53 per cent. was found instead of 104.50.

Lithium carbonate, prepared from lepidolite, was dissolved in hydrochloric acid; all metals except magnesium were separated by treatment successively with sulphuretted hydrogen, ammonia, ammonium sulphide, and small quantities of ammonium carbonate. The magnesium was completely separated by boiling with lithium hydrate, prepared by the action of silver oxide on the chloride. The solution was then considerably concentrated by evaporation, and precipitated by ammonia and ammonium carbonate: the lithium carbonate was boiled 20 times with small quantities of water to free it from chloride, then disseminated in a large quantity of cold water through which a stream of washed carbonic anhydride was passed. The clear filtered liquid was boiled, and the precipitated lithium carbonate several times



washed with boiling water and dried: no foreign substances could be detected in this salt.

The process of estimation was carried out as follows:—A known weight of this salt was dissolved in hydrochloric acid, and the solution was mixed with 10 times the weight of crystallised sodium phosphate and sufficient caustic soda to make it decidedly alkaline: it was then evaporated to dryness on the water-bath, and the residue was allowed to stand for 12 hours with sufficient 2·5 per cent. ammonia solution to dissolve all the soluble salts; the phosphate was then washed for a long time with dilute ammonia. The filtrate and wash-water were united and subjected twice to the same process after addition of a little caustic soda; the third treatment yielded only 0·6 mgrm. of phosphate. All evaporations were conducted in platinum, but the ignited phosphate left 7·7 mgrm. of silica on solution in hydrochloric acid, the silica probably arising from the caustic soda.

Lengthened washing of the precipitated phosphate with dilute ammonia is indispensable. Lithium orthophosphate dissolves when boiled with ammonium chloride solution with evolution of ammonia, and its purity may thus be ascertained. The decomposition which occurs is as follows:— $\text{Li}_3\text{PO}_4 + 2\text{NH}_4\text{Cl} = \text{LiH}_2\text{PO}_4 + 2\text{LiCl} + 2\text{NH}_3$ .

*Lithium metaphosphate* was obtained by evaporating the solution of lithium carbonate in excess of phosphoric acid. The most suitable proportions are two molecules of lithium oxide to three of phosphoric anhydride. When the temperature during evaporation reaches  $130^\circ$ , a soluble crystalline salt separates, which contains  $6\text{Li}_2\text{O} \cdot 5\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , it consists of ortho- and pyro-phosphate. On continuing the evaporation, this salt redissolves, and as soon as excess of metaphosphoric acid begins to be evolved as white fumes the lithium metaphosphate crystallises: the thick mass is boiled with water, and the metaphosphate remains as an insoluble heavy powder. The crystals are large or small according as more or less than the above proportion of phosphoric acid has been employed. It is probably a monometaphosphate.

This process also yields the sodium and potassium metaphosphates in a crystalline condition.

Analysis of the lithium salt by the method of Kraut, Nahnsen, and Cuno (*Annalen*, 182, 165) proved its composition to be that of lithium metaphosphate.

Lithium metaphosphate is a white crystalline powder, consisting of well-formed microscopic tables. It is insoluble in boiling water, slightly soluble in acetic acid, and easily soluble in hydrochloric, nitric, sulphuric, and phosphoric acids. Its sp. gr. is 2·461. At an incipient red heat, it melts to a colourless hygroscopic glass of 2·226 sp. gr., which is soluble in water with feebly acid reaction, and insoluble in alcohol.

*Lithium pyrophosphate* was prepared by dissolving Kraut's (*loc. cit.*) sodium lithium pyrophosphate in acetic acid and precipitating with alcohol: the bulky precipitate was washed with alcohol and dried. The salt contains  $2\text{H}_2\text{O}$ ; heated to  $100^\circ$  it loses 7·03 per cent., and if melted 14·55 per cent. of water. The salt dried at  $100^\circ$  is still pyrophosphate.

F. C.

**Estimation of Ferrous Oxide in Presence of Organic Acids or Sugar.** By J. M. EDER (*Ber.*, 13, 502—506).—Ferrous oxide can be accurately determined in mixtures containing organic acids by means of the reducing properties of potassium-ferrous oxalate. Neutral potassium oxalate is added to the solution, which should not contain a large quantity of free mineral acid. Excess of silver nitrate and ammonia are then added to the mixture. Metallic silver is precipitated in the proportion of 1 atom of silver for each molecule of ferrous oxide present,  $2\text{FeO} + \text{Ag}_2\text{O} = \text{Ag}_2 + \text{Fe}_2\text{O}_3$  (after the addition of the silver nitrate the liquid should be protected from direct sunlight). The precipitate consisting of metallic silver and ferric hydrate is collected on a filter, washed, dissolved in nitric acid, and the silver precipitated as chloride. If the liquid contains sufficient tartaric acid to prevent the precipitation of ferric hydrate, the silver may be weighed directly as metal. If the precipitate of metallic silver does not filter clear, ammonium chloride is added to the mixture.

W. C. W.

**Valuation of Pyrites by the Gravivolumetric Method.** By A. HOUZEAU (*Compt. rend.*, 90, 870—872).—1 gram of finely powdered pyrites is fused in a platinum crucible with 4 grams of pure potassium nitrate and 3 grams of pure sodium carbonate. The saline mass is dissolved in warm water, filtered to separate ferric oxide, and the solution diluted to 500 c.c. 10 c.c. are withdrawn, acidified with acetic acid, and the sulphuric acid estimated by means of a standard solution of barium chloride, measured by a *gravivolumeter*, in which the standard solution is weighed. Results accurate. C. H. B.

**Electrolytic Estimation of Cobalt, Nickel, and Copper.** By W. OHL (*Zeits. Anal. Chem.*, 1879, 523—531).—After enumerating the sources of error and inconvenience in the estimation of these metals by any but the electrolytic process, the author describes his method of procedure. The current was produced by a small Gramme machine, the rate of revolution of which was under control; a moderate speed producing a current which caused a deflection of  $70^\circ$  on an interposed sine-compass. When nickel is to be deposited in the presence of little or no cobalt, a very strong current is necessary, but if the quantity of cobalt is large, a weaker current must be employed to secure a firmly adherent deposit. Copper may be separated by means of a very strong current if it does not exceed 400 mgrs. in weight. The metal should be deposited on a platinum cone formed by rivetting the parts together, any folding together or curving of the edges being avoided, as they tend to retain the metallic deposit.

As an example of the application of the electrolytic process, the analysis of a cobalt-nickel ore is given. After decomposing the ore by heating it with strong nitric acid or aqua regia, preceded if necessary by fusion with sodium carbonate, the solution is evaporated to dryness; the residue is then dissolved in a little strong hydrochloric acid, diluted, and sulphuretted hydrogen passed through the hot solution until it is cold: the passage of the gas through the hot solution should be repeated, when all arsenic and copper present will settle rapidly as sulphides. If by the colour of the precipitate copper

is judged to be absent, the excess of sulphuretted hydrogen should be removed by heat before filtering, since arsenic sulphide is somewhat soluble in a solution of this gas. If copper sulphide is present, the removal of the gas is omitted, and a slight error arises from the arsenic sulphide present in the filtrate.

The filtrate is evaporated with addition of a little potassic chlorate to oxidise the iron: the residue is taken up with dilute hydrochloric acid, soda is then added to alkaline reaction, and the precipitate dissolved by addition of acetic acid; the liquid is then diluted and heated to boiling to precipitate the iron. The filtrate from the iron is evaporated to dryness, and the residue dissolved in water and dilute sulphuric acid, mixed with excess of ammonia and subjected to electrolysis; as soon as the liquid has been free from colour for some time, and a few drops yield no precipitate or dark coloration with ammonium sulphide, the platinum cone with the deposit of nickel and cobalt is removed, washed with water, then with absolute alcohol, dried by holding it over a heated surface and weighed. The nickel is then estimated in the dry way by Plattner's method, and the cobalt found by difference. This method of estimating the nickel is liable to an error of only 0.2 per cent.: the alternative plan is to dissolve the electrolytic deposit in dilute nitric acid, and separate the cobalt with potassium nitrite.

The precipitate of basic ferric acetate is free from nickel and cobalt or contains mere traces of those metals; and even if the iron should not be completely precipitated, a small amount of ferric hydrate precipitate present during electrolysis is harmless.

The separation of nickel, cobalt, and copper from the solution of any substance is effected by passing sulphuretted hydrogen slowly into the cold solution, which has been freed from silicic acid, until the copper sulphide separates; the arsenic remains almost entirely in solution: the copper precipitate is filtered off rapidly, and with the filter is heated with nitric acid, then evaporated to dryness; the residue is dissolved in nitric acid, diluted, and the copper precipitated by electrolysis: any arsenic present separates after the copper, the current is therefore stopped when the copper is completely separated, and the solution, freed from nitric acid by evaporation, is mixed with the former filtrate, from which the arsenic is then precipitated as sulphide and estimated as ammonium magnesium arsenate. Iron, if present in any quantity, is precipitated as basic ferric acetate, and nickel and cobalt are then separated from the ammoniacal solution by electrolysis, any ferric hydrate precipitate which forms on addition of ammonia being added to the iron precipitate. The alkaline earths can be determined in the liquid from which the nickel and cobalt have been separated.

Zinc is the only metal which need be separated before estimating nickel and cobalt. It must be separated by passing sulphuretted hydrogen into the acetic acid solution; the filtrate is evaporated, the residue dissolved in dilute sulphuric acid, and the ammoniacal solution is then electrolysed.

Copper is separated from arsenic as described above: antimony should be removed by twice evaporating with nitric acid: and lead, if

present in any quantity, should be precipitated as sulphate; traces of lead will not interfere, since the metal separates as peroxide on the positive pole. Silver is separated as chloride, and bismuth as basic chloride.

The author's experience in the application of the electrolytic method to the quantitative analysis of metal ores leads him to recommend it on the grounds of economy of time and great accuracy. F. C.

**Blowpipe Assay of Silver Lead.** By F. M. LYTE (*Analyst*, 1880, 99).—The inconvenience arising from the smallness of the silver button obtained in the assay of lead ores by the blowpipe, may be avoided by digesting 1 to 5 grams of the finely powdered ore with strong hydrochloric acid until all the lead is converted in chloride. It is then evaporated to dryness, and the residue is boiled with a concentrated salt solution (50—60 c.c. for each gram of ore taken). The solution containing the lead and silver chlorides is filtered, and the residue washed with boiling salt solution. Pieces of spongy lead (precipitated from lead acetate by zinc) are placed in the hot solution, and digested on the water-bath for a few hours; these precipitate and absorb the silver, becoming changed in colour to silver grey. The end of the reaction is known by no change of colour taking place in freshly added lead sponge. The lead is collected, heated with sodium carbonate on charcoal, and finally cupelled before the blowpipe.

L. T. O'S.

**Volumetric Analysis of Red Lead.** By F. LUX (*Zeits. Anal. Chem.*, 1880, 153—155).—By treating plumbic peroxide with an aqueous solution of oxalic acid in excess, decomposition takes place with formation of plumbic oxide, water, and carbonic anhydride. Warm dilute nitric acid dissolves the plumbic oxalate formed by the excess of oxalic acid originally used, and the quantity of the latter may be easily determined in the nitric acid solution. The author applies this method in conjunction with that of titrating lead by means of potassium dichromate in an acetic acid solution, for the ready determination of the practical value of red lead. Details of the method are given in the original paper. D. B.

**Presence of Arsenic in the Atmosphere.** By H. C. BARTLETT (*Analyst*, 1880, 81—82).—Experiments were made to show that arsenic would be present in the atmosphere of a room papered with an arsenical wall-paper. By placing the paper in a jar through which a current of pure hydrogen was passed containing a small quantity of ammonia, and directing the effluent gas on to a piece of filter-paper moistened with slightly acid silver nitrate solution, a deep brown mark is produced. In blank experiments, no mark appeared on the prepared paper. Hydrogen evolved from sodium amalgam and water is the most convenient to use, since that from zinc and sulphuric acid, even when it gives no reaction with Marsh's test, is liable to contain minute traces of arsenic and antimony.

L. T. O'S.

**Volhard's Permanganate Method of Titrating Manganese.** By A. E. HASWELL (*Dingl. polyt. J.*, 235, 387—391).—The author

mentions that this method surpasses all recent improvements made in this direction. He has carefully investigated the method, and finds it quick and convenient in execution, and the results very accurate. The method is based on the following facts. By treating a dilute solution of a salt of manganous oxide heated to  $100^{\circ}$  with a few drops of a solution of zinc sulphate, coloured pink by a few drops of a solution of potassium permanganate, and adding a solution of potassium permanganate drop by drop to the mixture, with constant agitation, the separation of a brown peroxide mixed with zinc oxide occurs in the form of large flakes, which readily separate from the clear supernatant faintly pink coloured liquid as soon as all the manganese has been precipitated. If the pink colour of the clear solution no longer disappears after standing for some time and repeated heating at  $100^{\circ}$ , the reaction may be considered to be complete, and the total manganese contained in the solution to be precipitated as peroxide. From the number of c.c. of standard potassium permanganate used, the quantity of manganese can be calculated very easily. Volhard gives the solution a concentration of 2 mgrms. manganese in 1 c.c., consequently dissolves 3.833 grams crystallised potassium permanganate in 1 liter of water. The solution to be standardised for manganese should not contain more than 0.25 per cent. of manganese. Iron appears to interfere with the accuracy of the results. It is, however, recommended to separate this metal by precipitation with zinc oxide.

The standard solution of potassium permanganate is titrated by treating it with a solution of potassium iodide acidified with hydrochloric acid. The iodine equivalent of the active oxygen in the permanganate is immediately liberated, provided that excess of iodide is used, which may easily be recognised by the circumstance that no iodine separates from the brown solution. The iodine liberated is then estimated by means of sodium thiosulphate, &c. D. B.

**Must and Wine Analysis.** By R. ULBRICHT (*Landw. Versuchs.-Stat.*, 25, 5—24).—*Determination of Chlorine.*—With precautions, the gravimetric method gives good results. The liquid is diluted, treated with 5 per cent. of milk of lime, and after an hour the solution is filtered off, heated to  $70^{\circ}$  with nitric acid and slight excess of silver solution, and the precipitate is washed with precaution and weighed.

*Determination of Sulphuric Acid.*—Very exact results can be obtained with care. The filtrate and wash water from the lime precipitate are mixed and acidified with a little hydrochloric acid, heated to boiling, and a very slight excess of barium chloride is added, the whole warmed for 2 hours, and then allowed to stand for 36 hours.

J. T.

**Examination of Sugar-beet and the Amount of Sugar the Roots contain.** By F. SCHULZE (*Bied. Centr.*, 133—135).—If during the expression of the juice from sugar-beet the amount of sugar present be estimated in the different portions, it will be found that the first and last portions contain the smallest quantities. When Scheibler's diffusion process is employed, the whole amount of sugar in the root can be determined, and if from this the amount of sugar in the juice be subtracted, the difference is the sugar retained in the mark. When

the root was sliced, a juice poorer in sugar was obtained by pressure; but these slices when pressed yielded a juice which when examined at different stages of pressing, contained more sugar in the first portions.

E. W. P.

**Scheibler's New Process for the Determination of Sugar in Beet.** By C. SCHEIBLER and others (*Biel. Centr.*, 1880, 136—143).—By the expression of the juice from the sugar-beet 4.5—5 per cent. of "mark" is left, so that up to the present time 95—95.5 per cent. have been the figures which were supposed to represent the true amount of juice in which the sugar was to be estimated. But this quantity is now shown to be considerably above the true quantity, which Scheibler and several others find to be only about 90 per cent. The excess is due to water forming a hydrate of the mark (colloïd water). The following process is recommended for the better extraction of the sugar. 20—25 grams of the crushed root are placed in a tube, the lower end of which is closed by a piece of felt. This tube is again enclosed in a larger tube ending in an upright condenser, the lower end of the outer tube being connected with a 50 cm. flask, in which is placed 25 c.c. of 95 per cent. alcohol. The alcohol is boiled, allowed to cool and run back through the tube containing the sugar-beet for three-quarters of an hour. At the end of the operation the fluid is filtered, and the sugar determined by the polariscope (see this vol., p. 144).

E. W. P.

**Separation of Fats from Soaps.** By J. WOLFF (*Zeits. Anal. Chem.*, 1879, 570—571).—In the ordinary method of soap analysis small quantities of unsaponified fats and resins are usually not estimated nor even detected. The author determines them by treating the soap with cold aniline, which does not dissolve soap, but readily dissolves fat and resin.

To free commercial aniline from benzene and nitrobenzene, several kilograms are mixed with a slight excess of hydrochloric acid, then diluted with 500 parts of water, and shaken until all aniline salt has been dissolved. The solution is then filtered through several thicknesses of well wetted filter-paper. The clear liquid is made just alkaline with sodium hydrate solution, and nearly saturated with sodium chloride. As soon as the aniline has separated it is run off and distilled, the portion boiling above 180° being preserved for use.

The finely divided soap is twice treated with about 20 parts of aniline for half an hour on the water-bath, being well stirred meanwhile, and hard particles being pressed. It is each time filtered when cold. The united aniline solutions are acidified with hydrochloric acid, mixed with four times their weight of water, stirred well, cooled, and shaken with ether. The clear ether solution is separated, the ether evaporated, and the residue of unsaponified fats and resins weighed.

F. C.

**Testing Butter.** By L. MEDICUS and S. SCHERER (*Zeits. Anal. Chem.*, 1880, 159—162).—Of the three methods recently published by Hehner, Reichert, and Koettstorfer for the determination of butter fat, Reichert's method appears to be the most useful and accurate, as

it determines that ingredient which distinguishes butter fat from other animal and vegetable fats of the same category, namely, the volatile acids.

The object of this paper was to see whether melted butter fat separates on cooling, so as to indicate to some degree any adulteration which may have taken place, and for this purpose Reichert's method was employed. It was found that the more difficultly fusible fat separated in places where the cooling first originated, whereas the more readily fusible fats separated towards the centre of the mass. The quantity of volatile fats had been increased in the centre and lower parts of the melted mass, whilst in the upper parts a decrease had taken place.

These experiments indicate the necessity of using the utmost care in sampling fatty substances for analysis. D. B.

**Woody Fibre Estimation and its Defects.** By C. KRAUCH (*Landw. Versuchs.-Stat.*, 25, 221).—After remarking on the unsatisfactory state of fodder analysis, and the want of accuracy in classing the results as protein, fat, non-nitrogenous extract, and woody fibre, the author details experiments made on residues obtained from rye grain, meadow hay, and red clover respectively, by treatment with ether and alcohol, cold and warm water, and infusion of malt. The residues were analysed, and were treated with dilute acids, potash solution, and Schulze's reagent in various orders, and the results are discussed without leading to any definite conclusions. J. T.

**Estimation of the Non-albuminoid Nitrogen in Fodder.** By E. SCHULZE (*Landw. Versuchs.-Stat.*, 25, 173—176).—Kern has shown (*ibid.*, 24, 368) that in Sachsse's method of estimating amides, the presence of ammonium salts causes error in the results, owing to the action of nitrous acid on these salts. On decomposing asparagine by means of nitrous acid, one-half its nitrogen is converted into ammonia, and this under the action of the acid increases the amount of nitrogen obtained, so that the result for asparagine is too high. The author finds that the amount of nitrogen obtained from ammonium salts depends on their state of concentration, and on the temperature at which the reaction takes place. J. T.

**Estimation of Proteids in Fodder.** By R. WAGNER (*Landw. Versuchs.-Stat.*, 25, 195—219).—In papers by F. Sestini (*ibid.*, 23, 305) and B. Dehmel (*ibid.*, 24, 214), the process given by the author is unfavourably criticised in part. The author gives numerous examples to show that the method he has previously described (*ibid.*, 21, 259) gives accurate results. The fodder may be extracted either by a 0.04 per cent. solution of hydrochloric acid or a 0.125 per cent. solution of potash; the latter gives the best results. The extraction takes a day, and should be made at the lowest possible temperature, with frequent shaking. The alkaline solution is treated with dilute acetic acid until a white precipitate appears, then a saturated solution of tannin in acetic acid is added to precipitate the proteids. After 12—24 hours filter, and to the filtrate add a considerable amount of common salt to

collect the proteids in suspension : after 24—48 hours this residue may be collected. J. T.

**Examination of Mineral Oils.** By O. BRENNEN (*Zeits. Anal. Chem.*, 1879).—The author describes his method of examining such oils as are used chiefly for lubrication of railway axles and of machinery. He claims for his process the advantage of detecting the presence of tar-oils, which resemble mineral oils in not being saponified by caustic soda solution; it also shows whether the oil is properly refined and is free from undissolved substances. The presence of undissolved particles in very small quantity is objectionable, since by settling they render the lower stratum of oil in a vessel useless for many purposes; they also clog the woollen feeder which supplies oil to railway axles.

The examination consists of the following parts:—

1. *Determination of the Specific Gravity.*

2. *Determination of the Temperature at which Vapour is Evolved which will Burn continuously.*—The oil is heated on a sand-bath in a porcelain crucible 6.4 cm. in diameter and 4.7 cm. deep, which is filled to within 1.2 cm. of its edge. A small flame is passed once over the top of the crucible without touching the edge or the surface of the oil; it should take as many seconds in passing as the number of cm. breadth of the crucible. This test is conveniently repeated for each 5° rise of temperature of the oil, and is then, if necessary, repeated for each 1° rise between the limits thus found. The oil should froth only slightly, or not at all, when thus heated.

3. *Determination of Solidifying Point.*

4. *Determination of Undissolved Bodies.*—10 c.c. of oil are dissolved in 10 c.c. of ether, filtered through a weighed filter, and the filter and residue weighed after having been washed with ether and dried.

5. *Behaviour with Soda Solution.*—5 c.c. of soda solution of 1.4 sp. gr. are poured into a graduated test-tube, 10 c.c. of oil are added, and the whole is well shaken and heated in a water-bath; the solution must separate perfectly from the oil in a few minutes or when the water boils; the tube is then removed and once more shaken and replaced in the water-bath; after the soda solution has once more perfectly separated it must be clear and show no alteration of volume after cooling; an increase of volume indicates unwashed tar-oils. The inside of the tube must be perfectly clean, to insure the rapid and complete separation of the solution from the oil.

6. *Behaviour with Nitric Acid.*—On mixing the oil with nitric acid of 1.45 sp. gr., the rise of temperature observed must be very slight, or better none; if much rise occurs, the presence of washed tar-oils is indicated. If a small preliminary trial shows that no very violent reaction occurs, 75 c.c. of oil are poured into a graduated 20 c.c. tube and are brought to 15° C.; 7.5 c.c. of the nitric acid at 15° C. are then added, the tube is closed with a cork through which a thermometer passes, and the liquids are well shaken. If a violent reaction occurs a larger vessel is used and a glass tube passes through the cork, which is closed with the finger during the agitation.

7. *Behaviour with Sulphuric Acid.*—This test is carried out in the



same way as that with caustic soda (5), 10 c.c. of oil being mixed with 10 c.c. of acid of 1.53 sp gr. The acid must not be coloured black or brown, otherwise insufficient refining is indicated, or the presence of tar-oils, already indicated by nitric acid, is confirmed.

8. *Examination of the Aqueous Extract for Slime and Free Acid.*—Water, which has been violently agitated with the oil, must separate clear and must show no acid reaction. Slimy particles will make the water turbid, they are not removed by filtration, and settle after a time.

The author does not consider the above method perfect, and intends to publish further papers on the reaction with nitric acid and on the determination of the consistency of the oil. F. C.

**Determination of Ash in Coal.** By F. MUCK (*Zeits. Anal. Chem.*, 1880, 131—149).—The determination and incineration of ash is in many cases accompanied with great difficulties, such as—

1. The difficulty of incinerating bodies like anthracite, graphite.
2. The formation of carbon, which cannot be burnt off without difficulty (with fusible organic substances).
3. The presence of certain mineral substances which retard the incineration, e.g. silica, phosphates, fusible salts
4. The tendency to decrepitate, shown by some plants and almost all kinds of coal.
5. The greater or less solubility of some ash-constituents.
6. The chemical changes which the ash may experience, according to the time and degree of heat and the draught of air.

The author has investigated this subject very fully, and gives a detailed account of his experiments, which tend to show that the following conditions should be observed in order to obtain accurate results:—

1. The substance to be incinerated must be pulverised very finely and heated very gradually.
2. In order to completely incinerate the ash it is advisable to moisten it with alcohol, after incineration, and to continue the burning.
3. Other conditions are considered in the original paper, which are, however, mostly known to practical analysts. D. B.

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## Technical Chemistry.

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**Potassium Ferrous Oxalate and its Use for Developing Photographic Bromide of Silver Plates.** By J. M. EDER (*Dingl. polyt. J.*, 235, 376—379).—Potassium ferrous oxalate has more powerful reducing properties than any acid or neutral ferrous compound hitherto examined, its power of reduction approaching that of an alkaline solution of pyrogallie acid. Hence it has been introduced in photography for developing bromide of silver plates. The author found that this developer, when applied correctly, gives better nega-

tives than those developed with the usual alkaline pyrogallic acid mixture. It is essential to use a solution of slightly acid reaction, otherwise the development of the plates will not be successful. Gelatin plates are at present mostly developed with this salt. The plates are dipped into a solution of potassium ferrous oxalate and the picture developed in about two to five minutes. Several plates can be placed and developed in the same solution. Since this solution is somewhat more expensive than pyrogallic acid, the author has been investigating various modes whereby the developer may be recovered. He succeeded in devising a method of recovering the most valuable ingredient of the solution, viz., potassium oxalate, by the very simple process of precipitating the iron with potash, evaporating and crystallising.

D. B.

**Analyses of Four Waters for Turin.** By A. LIEBEN (*Gazzetta*, 10, 86—115) and S. CANNIZZARO (*ibid.*, 115—118).—The municipality of Turin having decided to introduce a new water supply for the city, sent samples of four waters from different sources to the authors of these two papers for analysis. Lieben gives a long dissertation both on potable waters in general and on the methods of analysis, the analytical results being given in tabular form. The permanganate method (Schulze's process) was employed for the organic matter, as the author considers that of Frankland and Armstrong to be liable to error, both from loss of volatile organic matter during evaporation and from the action of the sulphurous acid. Cannizzaro's results agree with those obtained by Lieben, with the exception of the nitric and nitrous acid; the former chemist having taken all the precautions indicated by Kämmerer (*J. pr. Chem.*, 1875) found that no nitrous acid was present. Both chemists insist upon a knowledge of the history of the water as a most important factor in pronouncing an opinion as to its potability.

C. E. G.

**A Peculiar Water.** By W. WALLACE (*Analyst*, 1880, 79).—This deep well water, which penetrates the strata of sedimentary rocks of the lower coal formation, is entirely free from sulphates, but contains large quantities of free ammonia, of chlorine, and of barium, giving a precipitate with calcium sulphate. The analysis gave the following results in parts per million:—

|   |                     |                                      |                     |                          |                  |
|---|---------------------|--------------------------------------|---------------------|--------------------------|------------------|
| BaCO <sub>3</sub> .                             | CaCO <sub>3</sub> . | MgCO <sub>3</sub>                    | CaCl <sub>2</sub> . | MgCl <sub>2</sub>        |                  |
| 54.1  | 202.6               | 23.0                                 | 92.4                | 78.0                     |                  |
| KCl.  | NaCl.               | Al <sub>2</sub> O <sub>3</sub> , &c. | SiO <sub>2</sub> .  | Organic<br>and volatile. | Total<br>solids. |
| 24.0  | 1783.0              | 8.0                                  | 7.0                 | 85.0                     | 2417.1           |
| Hardness, degrees per million .....             |                     |                                      |                     |                          | 537.00           |
| Oxygen required to oxidise organic matter ..... |                     |                                      |                     |                          | 1.67             |
| Ammonia, free, per million .....                |                     |                                      |                     |                          | 0.95             |
| ,, organic .....                                |                     |                                      |                     |                          | 0.07             |

One month later the water had not altered in its composition, notwithstanding large quantities had been withdrawn from the well.

L. T. O'S.

**Evolution of Carbonic Oxide from Red-hot Iron Stoves.** By F. FISHER (*Dingl. polyt. J.*, 235, 438—443).—This question was first considered by Pettenkofer in 1851, and Morin in 1869 proved that iron stoves evolve carbonic oxide, which escapes into the air of the room when they are heated to redness, thus becoming injurious to health. The presence of carbonic oxide and hydrogen in the air heated by iron stoves is explained by the diffusion of these gases through the red-hot metal, which can be avoided by lining the interior of the stoves with refractory bricks or stone and regulating the fire so as to prevent the formation of carbonic oxide in the stove as much as possible. D. B.

**Mode of Desulphurising the Crude Soda-lyes obtained in the Le Blanc Process.** (*Dingl. polyt. J.*, 235, 299.)—The oxidation of the sulphides in the soda-lyes has recently been facilitated by the addition of manganese. 1 liter of the lye is treated with 1 gram of manganous chloride at a temperature of 50° to 60°. A strong current of air is then passed through the mixture, the manganous oxide formed being converted into a higher stage of oxidation, which, however, immediately gives up again its oxygen to the metallic sulphides in the lyes. As soon as these are desulphurised they are drawn off from the manganese oxide, which can be used for fresh quantities of the lye. In this way considerable quantities of the latter can be desulphurised, using comparatively little manganous oxide. D. B.

**Preparation of Soda from the Sulphate by Means of Lime and Sulphur.** By F. GUTZKOW (*Dingl. polyt. J.*, 236, 148—158). The author has patented a method of preparing caustic soda from sodium sulphate by treating the latter with calcium sulphite and introducing sulphurous acid gas into the mixture. Soluble calcium bisulphite is thus formed, which reacts with the sodium sulphate, forming calcium sulphate and sodium bisulphite. These are separated by filtration, and the gypsum washed out with hot water. The sodium bisulphite is then treated with milk of lime, whereby a solution of caustic soda is obtained, which contains a certain proportion of sodium sulphite and sulphate and also calcium sulphite. It is evaporated in the usual manner, and the calcium sulphite which is left after decantation is used in another operation. The following two questions presented themselves to the author in working out this method:—(1.) To what extent can sodium sulphate be transformed into the sulphite by means of lime and sulphurous acid; and (2) to what extent can sodium sulphite be rendered caustic by lime? As regards the first question, the conversion of sodium sulphate into sulphite is very satisfactory, and might be regarded as complete, if it were not for the solubility of the calcium sulphate, which is greater in the solution than in pure water. In the subsequent treatment with lime, this has a tendency to reconvert part of the sodium sulphite into sulphate. The second question could not be solved in a satisfactory manner, although success depends in a great measure on the solution being sufficiently dilute, but even with 14 grains per liter only 87 per cent. was converted. The results obtained, however, were only approximate, and, therefore,

could not be used as proper data for answering this question. It was found that sodium sulphite requires a greater dilution than the carbonate.

Details of the apparatus used and the mode of working are given. D. B.

**Dephosphorisation of Pig Iron.** By R. v. WAGNER (*Dingl. polyt. J.*, 236, 147).—Bull has recently discovered a process of dephosphorising pig iron, which depends on the conversion of the phosphorus into phosphoretted hydrogen. The process is said to have been very successful as far as it has been tried at the present time. It consists in introducing into the fluid metal, after separating carbon, silicon, &c., by means of a current of air, a stream of steam mixed with hot air. The steam is decomposed, the hydrogen combining with the phosphorus, and escaping in the form of vapour as phosphoretted hydrogen.

It is mentioned that this method, should it continue to give satisfactory results, would become of great practical importance, as it would probably compete with the Thomas-Gilchrist process. The author, however, points out that C. Winkler is really the originator of this idea. In the first part of his *Auleitung zur Untersuchung der Industrie-Gase* (Freiberg, 1876, 6) Winkler in describing the Bessemer process distinguishes (1) combustion of the carbon and silicon by means of a current of air, and (2) removal of phosphorus in the form of a hydrogen compound, by forcing superheated steam through the metallic column, which is identical with the process proposed by Bull. D. B.

**Preparation of Nickel.** (*Dingl. polyt. J.*, 235, 444.)—According to Laroche and Prat, the composition of the nickel ore of New Caledonia is as follows:—

|    |                  |     |                                |     |                                |     |      |     |                  |     |    |                           |
|----|------------------|-----|--------------------------------|-----|--------------------------------|-----|------|-----|------------------|-----|----|---------------------------|
|    | SiO <sub>2</sub> | CaO | Al <sub>2</sub> O <sub>3</sub> | MnO | Fe <sub>2</sub> O <sub>3</sub> | CoO | NiO  | MgO | K <sub>2</sub> O | LiO | Cu | H <sub>2</sub> O combined |
|    | 41.0             | 3.0 | 7.0                            | 9.0 | 14.0                           | 1.3 | 8.9  | 6.0 | 1.1              |     |    | 8.7 = 100.00              |
| to | 46.0             | 0.5 | 1.3                            | 4.0 | 5.2                            | 0.0 | 17.3 | 9.0 | 0.7              |     |    | 16.0 = 100.00             |

The powdered ore is treated with an equal weight of sulphuric acid of 56° to 66° B. The mixture is boiled out with water and treated with a quantity of ammonium sulphate equivalent to the amount of nickel sulphate present. After concentration, nickel ammonium sulphate crystallises out, which when recrystallised, is obtained in a chemically pure form. The latter is boiled with an equivalent quantity of an alkaline oxalate, and the precipitate treated with sodium or potassium carbonate at 110°. The oxalic acid is thus recovered, and can be used again for a fresh operation, whilst the carbonate of nickel is reduced to the metallic state in the usual manner. D. B.

**Examination of the Effect of Hard and Soft Water on the Brewing of Beer.** By E. R. SOUTHEY (*Bierl. Centr.*, 1880, 145—147).—Composition of the worts (unhopped) prepared with distilled water, and with hard water containing 66.9 grains calcium sulphate, and 16.5 grains magnesium sulphate per gallon, was compared, the

result being that neither of the above salts in solution has any appreciable influence on the amount of extract obtained, or on the composition of that extract; but the wort prepared with hard water settles more quickly, and remains unfermented longer, than if it had been prepared with soft water. E. W. P.

**Amount of Sugar in Sorghum, Maize, and Melons.** By C. A. GOESSMANN (*Bied. Centr.*, 1880, 122—124).—The amount of sugar (cane and grape) contained in several varieties of the above plants at different periods of growth was estimated, and the result arrived at was that they are unfitted for the manufacture of sugar by reason of the small quantity which they contain. E. W. P.

**Formation of Fat in Ripening Cheese.** By O. KELLNER (*Landw. Versuchs.-Stat.*, 25, 39—46).—The author criticises the results of several investigators, and then gives results obtained by comparing the proportion of fat in chalk-like and fatty-looking cheese from the same block, with that of two of the unchangeable constituents, viz., phosphoric acid and lime. The amount of fat was almost the same, being slightly less, but not materially so, in the riper portion. Samples from an older cheese gave a similar pair of results. The melting points of the fats obtained from the same block were almost identical, the melting points of the fatty acids also; so that the fats were found to be the same in quality and quantity in ripe and in less-ripe cheese. J. T.

**Estimation of the Value of Grain.** By E. WOLLNY (*Bied. Centr.*, 1880, 116—120).—It is usual to estimate grain by its volume-weight, but this is shown to be a false method; the results of careful experiment are, that the volume-weight is not proportional to the size of the grain; with barley and wheat, it diminishes with the size of the grain, whereas with certain sorts of oats it increases as the size of the grain diminishes: the volume-weight of a mixture of large and small grains is a mean of the volume-weight of both sorts; the volume-weight of grains of like size is greater the less water they contain; it is likewise greater the riper the crop be, and also higher in the case of translucent wheat: the volume-weight of the grains of cereals of different varieties is different, and is independent of the size of the grain.

As the volume-weight cannot be taken as a true indication of the value of grain, neither can the specific gravity, which is less in proportion as the grain is riper, and contains more moisture.

The only true guarantee is the absolute weight of the grains. Of grains of like weight and size, those which are most globular, are the most valuable. E. W. P.

**Analysis of Various Tinned Foods.** By G. W. WIGNER (*Analyst*, 1880, 99—102).—From the analysis made of different American and Australian tinned meats and vegetables, the author considers them to be very slightly, if at all, inferior to raw meat and vegetables as articles of food. L. T. O'S.

**New Coal-tar Colouring Matters.** (*Dingl. polyt. J.*, 235, 316.)—Meister, Lucius, and Brüning prepare from secondary and tertiary amines of the aromatic compounds new colouring matters by the action of tri- and tetra-chloroquinone or of crude chloranil.

To prepare violet colouring matters, 1 part chloranil is added gradually with constant stirring to 2 parts dimethylaniline, and the mixture heated at 60° to 70° for some time. Blue colouring matters are formed by the action of chloranil on methyldiphenylamine. To obtain green colouring matters, chloranil is allowed to act on benzylated diphenylamine and its homologues, benzytolylphenylamine, &c.

Colouring matters are also obtained according to Herran and Chande by the action of nitrobenzene on mixtures of aniline and double metallic chlorides.

D. B.

**Some Analyses of Starchmakers' Residues.** By F. HOLZFLEISS (*Bied. Centr.*, 1880, 66).—The author has analysed two samples of these residues with the view of estimating their value as fodder; one sample was in the state in which it left the factory; the other had been put under pressure to extract all the water possible. The analyses of the wet and dry substances show a striking difference in the percentage of albuminous substances and carbohydrates: the former largely diminishing, the latter increasing in the dried substance, which is easily accounted for by the water carrying off the albumin. The employment of pressure in order to bring the substance into portable and marketable condition would not be found injurious, but when it is used for feeding purposes, it should in every case be supplemented by highly concentrated starchy foods.

The author compares the value of both with raw potatoes; taking the residue from one centner of these at 0.17 mark, the wet starch residue is worth 0.44 mark, the dry residue 1.15 marks.

J. F.

**On Explosives for Blasting, especially Nitroglycerine.** By B. C. NIEDERSTADT (*Dingl. polyt. J.*, 233, 75—78).—The most widely used dynamite is *Noble's kieselguhr dynamite*. When used in solid rock it has from 6 to 7 times the force of blasting-powder.

The "kieselguhr" in its natural state has the following percentage composition:—Insoluble silica, peroxide of iron, alumina, and calcium sulphate, 15.43; soluble silica, 77.30; water, 7.27. *Green kieselguhr* has the following percentage composition:—Insoluble silica, &c., 10.97; soluble silica, 62.92; organic matter, 17.76; water, 8.35. The kieselguhr is first burned in a furnace to destroy the organic matter and expel water. The mingling of the nitroglycerine with the burned earth is done by hand labour in wooden troughs lined with lead or india-rubber. The cartridges are prepared at the manufactory, of size corresponding with that usual for the bore-hole. The strongest cartridges are made with 75 per cent. nitroglycerine, the absorbent material being nitrocellulose or kieselguhr. The weaker sorts contain about 50 per cent. of nitroglycerine.

*Rhexite* consists of a mixture of 30 to 65 per cent. of nitroglycerine with saltpetre, chalk, and sawdust.

Recently there has been brought into use in mining a mixture of nitroglycerine and dissolved gun-cotton.

*Lithofracteur* consists of 52 per cent. of nitroglycerine, mixed with kieselguhr, coal, Chili saltpetre, and sulphur.

*Dualin* is better fitted for practical work than lithofracteur. It contains 50 per cent. of nitroglycerine, with sawdust and potassium nitrate.

The sp. gr. of dualin is only half that of dynamite, and it has per volume about 50 per cent. less explosive power. W. T.

#### Liquid for the Preservation of Botanical Preparations.

By J. NESSLER (*Landw. Versuchs.-Stat.*, 24, 275—277).—The author has used a 20 per cent. solution by volume of alcohol with 1—2 drops of an 8 per cent. solution of sulphurous acid in the form of acid calcium sulphite to every 200 c.c. of alcohol. This is suitable for green parts which are easily bleached; for roots which are brown, 3—4 times as much of sulphurous acid is used. The solution has behaved very well since 1875. So far as observations go, animal preparations may be preserved in the same way. J. T.

#### Primavera-wood. By J. MOELLER (*Dingl. polyt. J.*, 236, 146).

—This wood comes from Navidad (west coast of Mexico), and was obtained by Exner in Hamburg, where it had been sent into the market as furniture-wood.

The author has examined this wood. As to its botanical origin nothing is known, and from its anatomical structure also sufficient data could not be obtained for tracing its origin. The colour of the wood is yellow on its split or sawn surfaces; its polished sections, however, are coloured light reddish-brown, and the naked eye discerns elegantly marked rays of a light colour, in which minute yellow spots are scattered about. The sp. gr. of the wood is 0.99, and its hardness very great. D. B.

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## General and Physical Chemistry.

**New Hydrogen Lines and the Dissociation of Calcium.** By H. W. VOGEL (*Ber.*, 13, 274—276).—The spectrum of hydrogen has been hitherto considered to consist mainly of four lines: but in his photographic examination of Geissler's tubes containing hydrogen, the author has detected a number of other lines, some of them in the violet and ultra-violet of remarkable intensity and sharpness. Almost the same lines are observed in the photographed spectrum of perfectly pure electrolytic hydrogen, and hence must be considered characteristic of that element.

One of the most brilliant of these lines is slightly less refrangible than the Fraunhofer line H', which, together with H'', is usually ascribed to calcium. The author designates it Hd<sub>4</sub>, the symbol Hd representing a hydrogen line.

According to Lockyer (*Proc. Roy. Soc.*, 28, 157), the element calcium, when submitted to the enormous temperature of the white fixed stars, which are regarded as the hottest, undergoes dissociation into two bodies X and Y, to which the lines H' and H'' respectively belong. This dissociation cannot be artificially effected. Lockyer relies on the observation of Huggins, that in the spectra of Sirius, Vega, and other stars, the first of these lines is present, while the other is absent or scarcely visible.

The author interprets the facts otherwise: the so-called H' line in the stellar spectra being, in his opinion, identical with the hydrogen line Hd<sub>4</sub>, and not belonging to calcium. The remaining hydrogen lines are also much more intense in these stellar spectra than in the spectrum of the sun.

This view is borne out by an examination of the published observations of Huggins (*Compt. rend.*, 1880, No. 2). Huggins there gives the wave-lengths of twelve stellar lines in the violet and ultra-violet. The first two of these are the acknowledged hydrogen lines, Hd<sub>4</sub> and Hd<sub>5</sub>; and the others agree so closely with the hydrogen lines discovered by the author, that there can be no doubt as to their identity with them.

| Huggins' stellar lines. | New hydrogen lines. |
|-------------------------|---------------------|
| 3968                    | 3968                |
| 3887.5                  | 3887                |
| 3834                    | 3834                |
| 3795                    | 3795                |
| 3767.5                  | 3769                |

The rest of Huggins' lines have not been observed by the author, who used glass prisms which strongly absorb violet and ultra-violet rays. Huggins used quartz prisms.

Whether these lines are contained in the solar spectrum must be ascertained by using more highly dispersive instruments. Doubtless the presence of the line H' will render difficult the detection of Hd<sub>4</sub>.



Lockyer explains the frequent occurrence of the line H' "injected into the chromosphere" without H'', observed by Young, as due to the dissociation of calcium. In the author's opinion the line noticed to occur singly by Young was H<sub>d</sub>, and not H'. Ch. B.

**Dichroic Fluorescence of Magnesium Platinocyanide.** By E. LOMMEL (*Ann. Phys. Chem.* [2], 8, 634—640).—A particularly well-formed crystal (a four-sided prism) of this salt being at the disposal of the author, various optical phenomena exhibited by it were carefully noted as follows:—

(1.) Viewed by reflected light, the side faces were green, the end faces blue-violet.

(2.) A ray of transmitted light was broken up into an ordinary bright carmine-red ray, and an extraordinary dark blood-red ray.

(3.) In ordinary blue or violet light, the crystal showed splendid orange fluorescence.

(4.) When this orange light is viewed through a Nicol prism it appears orange-yellow when the plane of polarisation of the Nicol is perpendicular to the axis of the crystal, scarlet when it is parallel to the same axis.

(5.) If the violet light employed be first polarised, the fluorescent light is orange-yellow when the plane of polarisation is perpendicular to, scarlet when it is parallel to the axis of the crystal.

(6.) If a polarised violet ray falls normally on one of the end faces, a scarlet fluorescent light is obtained, and this colour is unchanged when the plane of polarisation is turned about the axis of the crystal.

(7.) If the ray falls obliquely, the plane of polarisation remaining perpendicular to the end-face and therefore containing the axis of the crystal, the colour remains unchanged; if, however, the plane of polarisation be inclined to the axis, the colour changes. From this it would appear that the light vibrations must be perpendicular to the plane of polarisation. The same conclusion results from the following considerations:—Red fluorescent light is obtained when the violet ray falls normally on the end-face, and when consequently the plane of vibration is perpendicular to the axis of the crystal; red light is also obtained from the side-faces when the plane of polarisation is parallel to the axis of the crystal; but since, in the first case, the plane of vibration is perpendicular to the axis, it should be the same in the second: it is therefore perpendicular to the plane of polarisation.

F. D. B.

**Phosphorescence.** By B. STÜRTZ (*Ann. Phys. Chem.* [2], 8, 528).—In high vacua, the following substances exhibit phosphorescence:—Magnesium phosphate, wolframite, cerusite, adularia, double spar, apatite, franklinite, dolomite, red spinel, cobalt-glanz, stannite, baryta, chrome-ironstone, lazulite, lepidolite, zinnwaldite, ankerite, greenockite, pektolite, borax, leucite, sanidin, and the meteorite of Java, 1869. Cerusite is deprived of this property by ignition; while on the other hand the following substances exhibit no phosphorescence, or but a faint trace, until after they have been heated to redness:—Brucite, magnesite, orthoclase, kaolin, axinite, kieselzink, fergusonite, apophyl-

lite, and coelestin. A long list of minerals is also given which do not exhibit phosphorescence.

R. R.

**Electro-optic Observations on Various Liquids.** By J. KERR (*Phil. Mag.* [5], 8, 85—102 and 229—245).—Some years ago two papers were published by the author (*ibid.*, 1875) describing experiments in which a power of double refraction was induced in glass, carbon bisulphide, and other dielectrics by the application of electric force; since then observations have been made with improved apparatus, and with the advantage of previous experience.

The liquid to be examined is contained in a glass cell formed by boring a hole one inch in height and five-eighths of an inch in width through a piece of plate-glass three-quarters of an inch thick; the ends of the hole are covered with thin pieces of plate-glass gently pressed against the main piece by suitable screws. In the centre of the cell thus formed two brass buttons, each one-quarter of an inch in diameter, oppose their slightly convex and heavily plated surfaces. The distance between the two surfaces is one-eighth of an inch, whilst the line joining their centres is horizontal and parallel to the surfaces of the plate-glass. One of the buttons is connected with an electrical machine, the other with the earth by means of wires passing through holes drilled in the glass. Similar holes serve to fill and empty the cell. A ray of light emitted by a flat paraffin flame presented edgewise, passed, first through a polarising Nicol having its principal section at an angle of  $45^\circ$  to the horizon, then through the cell above described, then through one or more slips of thin plate-glass so arranged that they could be subjected to strain by means of weights, and finally through the analysing Nicol.

In order thoroughly to understand the results of these experiments, we must remember that when a ray of light polarised in a plane inclined at  $45^\circ$  to the horizon passes through a slice of a uniaxial crystal having its principal axis vertical, the ray is broken up into two parts, one of which (the ordinary ray) has its vibrations in a plane perpendicular to the axis; the other (the extraordinary ray) has its vibrations in a vertical plane containing the axis. In negative uniaxial crystals, such as calcspar, the velocity of the extraordinary ray is greater; in positive uniaxial crystals, such as quartz, it is less than that of the ordinary ray. Precisely the same effect can be obtained with a piece of glass subjected to strain in one direction; if stretched vertically or compressed horizontally, the light, having its vibrations vertical, will travel faster; if compressed vertically, or stretched horizontally, the light, having its vibrations vertical, will travel slower than that which has its vibrations horizontal. In the first case, therefore, the glass acts as a negative, in the second, as a positive uniaxial crystal, with the principal section vertical.

Since this birefringent action induced in the glass varies with the strain to which it is subjected, it is evident that we are provided with a means of exactly compensating any similar action of the electrified liquid in the cell, and so observing the nature and measuring the amount of such action. This is the object of the slips of glass placed in the path of the ray of light, as above described.

As an illustration of the effects observed when a liquid is submitted

to electric force, we may select those obtained with carbon bisulphide. The cell being filled with this liquid, the slips of glass being subjected to no strain, and the analysing Nicol being turned to perfect extinction, the electrical machine is set in motion, and immediately the light is restored in the form of a fine vertical line; as the potential rises, the light increases steadily until it is quite brilliant; but if a spark be taken upon the knuckle from the prime conductor the phenomenon vanishes instantly. One of the compensating slips is now subjected to strain, and it is found that horizontal tension strengthens the effect of electrical action, whilst horizontal compression weakens it, and when strong enough reproduces sensibly perfect extinction. It would, therefore, seem that the electric tension has the same effect on the liquid as a horizontal tension on the glass, in other words, the electric force sets up a birefringent action in the carbon bisulphide; the light which is polarised in the plane parallel to the lines of force, that is to say, the vibrations of which take place in the plane perpendicular to the lines of force, is relatively retarded.

Carbon bisulphide when electrified acts therefore as a positive uniaxial crystal with the axis perpendicular to the lines of force. Other liquids, such as colza and olive oils, with which the glass cell was filled, yielded opposite results, behaving as a negative uniaxial crystal with the axis in the same relative position.

Experiments were made with a large number of liquids, with the general results given in the following table, where the positive liquids are arranged as nearly as possible in the descending order of electro-optic power, the larger and clearer intervals being marked by separating lines. The negative liquids are not so arranged, but colza and seal oils are certainly among the strongest, and linseed is the weakest.

| Positive liquids.                          | Negative liquids.            |
|--|------------------------------|
| Carbon bisulphide, <i>v. g.</i>            | <i>Vegetable fixed oils.</i> |
| <hr/> Cumene, <i>g.</i>                    | Colza, <i>v. g.</i>          |
| Paraffin oil (sp. gr. 0.890), <i>v. g.</i> | Sweet almonds, <i>v. g.</i>  |
| <hr/> Carbon dichloride, <i>v. g.</i>      | Olive, <i>v. g.</i>          |
| Xylene, <i>v. g.</i>                       | Poppy-seed, <i>g.</i>        |
| Toluene, <i>v. g.</i>                      | Rape-seed, <i>p. g.</i>      |
| Cymene, <i>v. g.</i>                       | Nut.                         |
| Benzene, <i>v. g.</i>                      | Mustard-seed, <i>p. g.</i>   |
| <hr/> Amylene, <i>v. g.</i>                | Linseed, <i>p. g.</i>        |
| <hr/> Paraffin oil, <i>v. g.</i>           | <i>Animal fixed oils.</i>    |
| Sperm oil, <i>p. g.</i>                    | Seal, <i>g.</i>              |
| Terebene, <i>v. g.</i>                     | Cod liver.                   |
| Bromotoluene, <i>b.</i>                    | Lard, <i>p. g.</i>           |
| <hr/> Valeric acid, <i>b.</i>              | Neatsfoot, <i>g.</i>         |

As it is admitted that very slight changes in the conditions of the

experiment produce large variations in the electro-optic power, and as, moreover, no care seems to have been taken to obtain pure liquids, further than to purchase the best readily obtainable, the above order of the positive liquids may require much alteration.

The electrical conductivity of the various liquids was roughly estimated by drawing sparks from the prime conductor of the electrical machine, firstly when the conductor was in connection with one of the brass buttons of the cell, while the other was in connection with the earth; and secondly when the conductor was entirely disconnected. If the sparks are in each case of about the same density and length, the liquid in the cell must evidently be a good insulator; if the sparks are smaller in the first case the liquid is not a good insulator, whilst if no sparks at all can be obtained, the liquid evidently conducts electricity without difficulty. The letters *v. g.*, *g.*, *p. g.*, and *b*, placed after the names in the table, signify that the insulation obtained with the liquid is very good, good, pretty good, or bad.

When experiments were made with nitrobenzene, it was found that no optical effect could be obtained in the usual way, the liquid conducting electricity with the greatest facility. An interesting phenomenon was, however, observed when the wire connecting the machine with the cell was interrupted by a small air-space. In this case a momentary restoration of the light takes place at the instant of the passage of a spark across the air-space, and this restoration is the brighter the greater is the distance across which the spark has to travel.

By means of a Thomson's long-range electrometer, the electric potential during the experiments with non-conducting liquids was measured, and the tension of the compensating glass slips being at the same time noted, it was possible to obtain at any rate a general idea of the relation between potential and birefringent action. As regards the glass slips, it was inferred that the straining weight and the optical effect are sensibly proportional as long as the weight does not exceed 12 lbs. The weight, therefore, may be regarded as a measure of the optical effect. This being so, quantitative experiments with carbon bisulphide proved that as the potential increases the intensity of the corresponding birefringent action also increases, and that the increments of potential corresponding to a constant increment of birefringent action have sensibly smaller values at high than at low potentials. Experiments with other liquids gave similar results, and it was remarked that in some cases the optically equivalent potentials for two liquids were respectively proportional. F. D. B.

**Specific Heat of Water.** By BAUMGARTNER (*Ann. Phys. Chem.* [2], 8, 648—653).—At Prof. Pfaundler's suggestion, new determinations were made, in which the method of mixtures was employed, precautions being taken to render the results as accurate as possible. Tables of the numbers obtained are given. The values of the true specific heat of water at 100° (the specific heat at 0° being taken as unity) as given by different observers are as follows:—

|   |        |
|---|--------|
| Regnault's experiments and calculation .....                      | 1·0130 |
| "                    "            and Bosscha's calculation ..... | 1·0220 |
| v. Munchhausen's experiments and Wüllner's calculation....        | 1·0302 |
| Baumgartner's experiments and Pfaundler's calculation ....        | 1·0307 |
| Henrichsen's experiments and calculation .....                    | 1·0720 |
| Jamin and Amaury's experiments and calculation .....              | 1·1220 |
| Marie Stamo's experiments and calculation .....                   | 1·1255 |

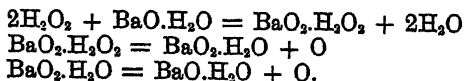
F. D. B.

**Freezing Mixtures of an Acid and a Hydrated Salt.** By A. DITTE (*Compt. rend.*, 90, 1163—1165).—The reduction of temperature observed when sodium sulphate is mixed with hydrochloric acid is not due simply to the solution of the salt. Double decomposition takes place in accordance with the principle of maximum work; sodium chloride is produced, and this, being insoluble in concentrated hydrochloric acid, is precipitated: the water which existed in the salt as a solid is set free as a liquid, and it is mainly this passage of the water from the solid to the liquid condition which causes an absorption of heat. If the hydrochloric acid be not sufficiently concentrated, a portion of the salt formed is dissolved, the decomposition is not complete, and the maximum reduction of temperature is not obtained. When 16 parts of sodium sulphate are mixed with 12 parts of the commercial acid, the temperature of the mixture is reduced about 33°. Similar effects are produced with mixtures of sodium phosphate or sulphate with nitric acid, and the alums or sodium phosphate with hydrochloric acid.

Pure phosphoric acid may be easily obtained by saturating a solution of sodium phosphate with hydrochloric acid gas, decanting the clear liquid from the precipitated common salt, and distilling off the excess of hydrochloric acid.

C. H. B.

**Compounds of Hydrogen Peroxide.** By BERTHELOT (*Compt. rend.*, 90, 334—337).—The paper gives the measurements of the thermic relations of certain combinations of hydrogen peroxide with alkalis, recently discovered by Schöne. The combination  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ , decomposes with development of heat = + 14·2 cal. into  $\text{BaO}_2 \cdot \text{H}_2\text{O} + \text{O}$ ; this hydrate of barium peroxide then combines with more water,  $\text{BaO}_2 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O} = \text{BaO}_2 \cdot 10\text{H}_2\text{O} = + 29·6$  cal., and finally it breaks up into  $\text{BaO} \cdot \text{H}_2\text{O}$  and oxygen,  $\text{BaO}_2 \cdot 10\text{H}_2\text{O} = \text{BaO} \cdot 10\text{H}_2\text{O} + \text{O} = + 11·8$  cal., each of these reactions being attended with development of heat. The same series of reactions serves to explain the instability of hydrogen peroxide in the presence of a trace of baryta, or of any other alkali, the following series of reactions taking place:—



All these reactions are attended with a disengagement of heat, and thus the alkali reverts to its original condition, when it reacts upon a fresh quantity of hydrogen peroxide, continuing a series of reactions which individually and collectively are exothermic.

R. R.

**Heat of Formation of Ammonia, of the Oxides of Nitrogen, and of the Nitrates.** By J. THOMSEN (*Ber.*, 13, 498—500).—Berthelot (*Compt. rend.*, 89, 877, this volume, p. 207) has recently shown that the heat of formation of ammonia cannot be accurately deduced from experiments based on the action of chlorine on aqueous ammonia. Satisfactory results are obtained by burning ammonia in oxygen; the heat of combustion for 1 mol.  $\text{NH}_3$  equals 91300. The heat of formation of  $\text{N} + \text{H}_3$  is 12200.

The author has repeated Berthelot's experiments, and obtains 90650 for the heat of combustion, and 11890 as the heat of formation for 1 mol.  $\text{NH}_3$ .

Since the heat of formation of ammonia enters into the calculations for the heat of formation of the acids and oxides of nitrogen, the following numbers must be substituted for those contained in the previous communication (*Ber.*, 13, 498—500, and this vol., 81).

TABLE I.

|                       | Reaction.  | Heat of formation. |
|-----------------------|--|--------------------|
| Nitrous oxide .....   | $\text{N}_2 + \text{O}$                                | -18320             |
| " " .....             | $\text{N} + \text{NO}$                                 | + 3255             |
| Nitric oxide.....     | $\text{N} + \text{O}$                                  | -21575             |
| " " .....             | $\text{N}_2\text{O} + \text{O}$                        | -24830             |
| Nitrous acid.....     | $\text{N}_2 + \text{O}_3 + \text{Aq.}$                 | - 6820             |
| " " .....             | $\text{N}_2\text{O}_2 + \text{O} + \text{Aq.}$         | -36830             |
| " " .....             | $\text{N} + \text{O}_2 + \text{H} + \text{Aq.}$        | +30770             |
| " " .....             | $\text{NO} + \text{O} + \text{H} + \text{Aq.}$         | +52345             |
| Nitrogen dioxide..... | $\text{N} + \text{O}_2$                                | - 2005             |
| " " .....             | $\text{NO} + \text{O}$                                 | +19570             |
| Nitric acid .....     | $\text{N}_2 + \text{O}_5 + \text{Aq.}$                 | +29820             |
| " " .....             | $\text{N}_2\text{O} + \text{O}_4 + \text{Aq.}$         | +48140             |
| " " .....             | $\text{N}_2\text{O}_2 + \text{O}_3 + \text{Aq.}$       | +72970             |
| " " .....             | $\text{N}_2\text{O}_4 + \text{O} + \text{Aq.}$         | +33830             |
| " " .....             | $\text{N} + \text{O}_3 + \text{H}$                     | +41510             |
| " " .....             | $\text{NO} + \text{O}_2 + \text{H}$                    | +63085             |
| " " .....             | $\text{NO}_2 + \text{O} + \text{H}$                    | +43515             |
| " " .....             | $\text{N}_2\text{O}_4 + \text{O} + \text{H}_2\text{O}$ | +18670             |
| " " .....             | $\text{N} + \text{O}_3 + \text{H} + \text{Aq.}$        | +49090             |
| " " .....             | $\text{NO} + \text{O}_2 + \text{H} + \text{Aq.}$       | +70665             |
| " " .....             | $\text{NO}_2 + \text{O} + \text{H} + \text{Aq.}$       | +51095             |
| " " .....             | $\text{NO}_2\text{HAq.} + \text{O}$                    | +18320             |

TABLE II.—Heat of formation of Metallic Nitrates by direct union of their Elements.

| Anhydrous nitrates. | Heat of formation. | Anhydrous nitrates. | Heat of formation. |
|---------------------|--------------------|---------------------|--------------------|
| Potassium ....      | 119480             | Barium .....        | 225740             |
| Sodium .....        | 111250             | Strontium.....      | 219850             |
| Lithium .....       | 111620             | Calcium .....       | 203230             |
| Thallium .....      | 58150              | Lead .....          | 105500             |
| Silver .....        | 28740              |                     | W. C. W.           |

**Heat of Formation of Chloral Hydrate.** By A. WURIZ (*Compt. rend.*, 90, 337—342).—The experiments described in the paper lead to the following conclusions. The vapours of water and of anhydrous chloral may be mixed without giving rise to any sensible change of temperature. This fact supports the view entertained on other grounds that the vapour of chloral hydrate is a mixture and not a compound, and that it forms therefore no exception to the law of Avogadro and Ampère.

Sainte-Claire Deville considers that the experiments detailed in the foregoing paper do not determine the point at issue. He declines to accept either Avogadro's law, or any doctrine concerning atoms, molecules, forces, peculiar states of matter, &c., refusing to believe in what he cannot see or even imagine. As a matter of fact, the vapours of ammonium chloride, of the chlorides of the compound ammonias, and of many volatile organic bases, correspond with 8 vols., and it has not yet been proved that any one of these vapours is a mixture.

R. R.

**Heats of Combustion of Glycerol and of Ethylenic Glycol.** By W. LOUGUININE (*Compt. rend.*, 90, 367).—The heat of combustion of glycerol in the reaction  $C_3H_8O_3$  liquid + 70 gaseous =  $4H_2O$  liquid +  $3CO_2$  gaseous, is 392,455; that of ethylenic glycol in the reaction,  $C_2H_4O_2$  liquid + 50 gaseous =  $3H_2O$  liquid +  $2CO_2$  gaseous, is 283,293.

R. R.

**Volatile Metallic Chlorides.** By V. MEYER and H. ZÜBLIN (*Ber.*, 13, 811—815).—The authors have endeavoured to settle the question as to whether such chlorides as  $Fe_2Cl_6$ ,  $Sn_2Cl_4$ , become  $FeCl_3$  and  $SnCl_4$  at higher temperatures, and claim to have proved the existence of  $SnCl_4$  at a temperature of about  $800^\circ$ .

G. T. A.

**Compression of Gaseous Mixtures.** By L. CAILLETET (*Compt. rend.*, 90, 210).—When a mixture of air and carbonic anhydride is submitted to pressure, the liquefaction of the carbonic anhydride is often greatly retarded. Thus, a mixture of equal vols. of air and carbonic anhydride will support a pressure of 400 atmospheres at  $0^\circ$  without visible change. When, however, 5 vols. of carbonic anhydride are mixed with 1 vol. of air, the former is easily liquefied. If the pressure be then raised to 150 or 200 atmospheres, the meniscus of liquefied acid, before concave and well-defined, grows flat and indistinct, then it gradually becomes imperceptible, and the liquid at length disappears altogether. The tube then appears as if filled with homogeneous matter, which resists all further pressure as a liquid would.

When the pressure is again slowly diminished, the liquid suddenly reappears, at a pressure which is constant for given temperatures. A thick cloud appears in the tube, spreads, and vanishes as the liquid forms. The pressures at which the liquid carbonic anhydride reappears are at  $5.5^\circ$ , 130 atmospheres; at  $10^\circ$ , 124 atmospheres; at  $13^\circ$ , 120 atmospheres; at  $18^\circ$ , 113 atmospheres; at  $19^\circ$ , 110 atmospheres. Carbonic anhydride gas compressed beyond 250 atmospheres is not liquefied at  $21^\circ$ . It might be supposed that this disappearance

of the liquid is apparent only, in consequence of the refractive index of compressed air increasing more rapidly than that of liquid carbonic anhydride, so that at the point where the two indices become equal, the surface of the liquid would cease to be visible. But, in that case, the surface of separation should again become visible when the pressure is further increased. This, however, does not occur, and the author's conclusion is that under high pressures a gas and a liquid are capable of solution in each other, so as to form a homogeneous whole.

R. R.

*Note.*—The recent experiments of Ramsay on the so-called critical point of liquids (*Proc. Roy. Soc.*) would seem to require some modification of the above theory.—C. E. G.

**Variation of the Tension of Vapour emitted above and below the Point of Fusion.** By P. DE MONDESIR (*Compt. rend.*, 90, 1158—1161).—The variations in the tension of the vapour of a substance are so much greater above its point of fusion than below that the two series of variations cannot be accurately represented by the same curve.

C. H. B.

**Proportion of Carbonic Anhydride in the Air.** By J. REISET (*Compt. rend.*, 90, 1144—1148).—The mean of 91 day and night determinations made during the latter half of 1879 was 29.78 vols. of carbonic anhydride in 100,000 of country air. Between 9 A.M. and 4 P.M. the mean amount was 28.91 vols. in 100,000; during the night 30.84 in 100,000; i.e., the proportion of carbonic anhydride in the atmosphere is greater during the night than in the daytime. In foggy and hazy weather the mean amount was 31.66, with a maximum of 34.15 in a very dense fog. Details of the method of determination and of the apparatus employed are given.

The proportion of aqueous vapour in the air varied from 4.215 grams per cubic meter in November to 16.552 grams in August, the mean being 10.135 grams (see also this Journal, 36, 744).

The author considers that no connection has yet been definitely established between the variations in the proportion of carbonic anhydride in the air, and the mode of circulation of the latter.

C. H. B.

**The Problem of Estimating the Number of Isomeric Paraffins of the Formula  $C_nH_{2n+2}$ .** By F. HERMANN (*Ber.*, 13, 792).—The author gives no description of his method, but states that by a "more concrete method" than Cayley's (On the analytical forms called Trees. Report of British Association, 1875) he finds the possible number of isomeric paraffins of the formula  $C_{12}H_{26}$  to be 355.

G. T. A.

**History of Periodic Atomicity.** By L. MEYER (*Ber.*, 13, 259—265).



## Inorganic Chemistry.

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**Vapour-density of Iodine.** By F. MEIER and J. M. CRAFTS (*Ber.*, 13, 851—873).—The authors have repeated Victor Meyer's experiments (*Ber.*, 13, 399, and this vol., p. 433) on the density of iodine vapour, introducing slight modifications in the apparatus to increase the accuracy of their results, and they find that the vapour-density of iodine begins to be abnormal between 600° and 700°, and at a temperature of 1390° it is 0.60 of the theoretical density.

The difference between the results of V. Meyer and those of Deville and Troost (*Ann. Chim. Phys.*, 59, 161) is partly due to the fact that the latter authorities have taken the temperature of boiling zinc and cadmium as 1040° and 860° instead of 940° and 746.3° respectively.

W. C. W.

**Action of Potassium Iodide on Hydrogen Peroxide.** By E. SCHÖNE (*Ber.*, 13, 627—629).—The separation of the small quantity of free iodine which occurs on mixing pure hydrogen peroxide with neutral potassium iodide is not due, as stated by Berthelot (*Compt. rend.*, 90, 333), to the action of the carbonic acid in the air, or to some constituent of the containing vessel, but to the fact that hydrogen peroxide is decomposed by potassium iodide into water and oxygen, a small quantity of free iodine and free alkali being liberated at the same time (compare *Annalen*, 195, 228).

T. C.

**Decomposition of Hydrogen Peroxide in Presence of Alkalis and Alkaline Earths.** By E. SCHÖNE (*Ber.*, 13, 623—627).—The author considers that Berthelot's theory (*Compt. rend.*, 90, 334) of the decomposition of hydrogen peroxide in presence of alkalis or alkaline earths is incomplete, since it does not account for the yellow colour, which always accompanies the spontaneous decomposition of the double compounds of hydrogen peroxide with the peroxides of the alkalis and alkaline earths; and that his own view (*Annalen*, 192, 257; 193, 241), according to which the formation of higher oxides of the metal (tri-, tetra-, or even pentoxides) plays an important part in the decomposition of hydrogen peroxide in presence of the alkalis and alkaline earths, is more in accordance with observation.

T. C.

**Action of Sulphurous Anhydride on the Oxides of the Alkaline Earth-metals.** By K. BIENBAUM and O. WITTICH (*Ber.*, 13, 651—653).—*Barium oxide* unites slowly with sulphurous anhydride at 200°, and more rapidly at 230°, forming  $\text{BaSO}_3$ . *Strontium oxide* absorbs the gas less energetically than barium oxide, the reaction commencing only at 230°; the product is  $\text{SrSO}_3$ . *Calcium oxide* (compare Schott, *Dingl. polyt. J.*, 202, 52; and Rammelsberg, *Pogg. Ann.*, 67, 249) does not absorb the gas below 400°, but at this temperature combination takes place rapidly with the formation of a basic sulphite,  $\text{Ca}_2\text{S}_2\text{O}_7$ . At 500° the gas is very rapidly absorbed, but the sulphite then splits up into sulphate and sulphide. *Magnesium oxide* begins to

absorb the gas very slowly at  $326^{\circ}$ , forming  $\text{MgSO}_3$ , but this is decomposed at a slightly higher temperature. T. C.

**Persulphuric Acid.** By BERTHELOT (*Compt. rend.*, 90, 269—275, and 331—334).—The author describes in the first paper his recent study of the formation by electrolysis of persulphuric acid, which compound was discovered by himself in 1878. The most concentrated solution of persulphuric acid he could obtain had 123 grams of  $\text{S}_2\text{O}_7$  in 1 litre, the liquid consisting in addition of 375 grams of sulphuric acid and 850 grams of water. The method of operating was to pass the current from 9 Bunsen cells, connected to form 3 elements, through dilute sulphuric acid. The platinum electrodes were separated by a porous partition, and measures were adopted to prevent the temperature from rising. At a certain stage of concentration the character of the reaction is modified, and instead of pure persulphuric acid a combination of that substance with hydrogen peroxide is formed, tending to the definite composition,  $\text{S}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$ . This compound, the author considers, is analogous to the combination of barium and hydrogen peroxides,  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ , discovered by Schöne.  $\text{S}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$  is almost entirely changed into persulphuric acid when it is mixed with an excess of monohydrated sulphuric acid. Persulphuric acid in solution slowly decomposes; the excess of oxygen is gradually liberated, but a certain quantity of hydrogen peroxide is at the same time produced. The stability of the acid is increased by dilution.

In the second paper, the author gives the details of various thermic determinations relating to the heat of formation of persulphuric acid and other substances.

From these it appears that the formation of hydrogen peroxide, of persulphuric acid, and of ozone are endothermic, and form a graduated series:—

Ozone,  $\text{O}_2 + \text{O} = (\text{O}_3)$  gives  $-29\cdot6$  calories.

Persulphuric acid,  $\text{S}_2\text{O}_7 + \text{O} = (\text{S}_2\text{O}_7)$  absorbs  $27\cdot6$  calories.

Oxygenated water,  $\text{H}_2\text{O} + \text{O} = (\text{H}_2\text{O}_2)$  absorbs  $21\cdot6$  calories.

These substances are transformable one into another, and they all contain active oxygen, that is to say, oxygen which acts on oxidisable bodies more readily than ordinary oxygen. This is explained by the excess of energy which is stored up in them, as indicated by their thermic relations. R. R.

**Constitution of Selenious Acid.** By A. MICHAELIS and B. LANDMANN (*Ber.*, 13, 656—657).—The fact that iodides of the alcohol radicles act on sulphites with formation of sulphonic acids shows that sulphurous acid may be considered as hydrogen sulphonic acid,  $\text{H}\cdot\text{SO}_2\text{OH}$ . The following experiments have been made with the object of determining whether selenious acid has a similar constitution. Ethyl iodide acts on potassium selenite only at high temperatures, forming free selenium, potassium iodide, and alcohol; in a similar manner by the use of benzyl chloride we obtain free selenium, potassium chloride, benzaldehyde, and a little benzoic acid. Under these circumstances, therefore, selenious acid acts as an oxidising agent.

Sodium ethylate and sulphurous chloride give  $\text{SO}(\text{OEt})_2$ , whilst ethyl iodide and silver sulphite give  $\text{Et}.\text{SO}_2.\text{OEt}$ ; the corresponding compounds of selenium, on the contrary, give the same product in both cases, viz.,  $\text{SeO}(\text{OEt})_2$ , which is decomposed by water, forming selenious acid. The above reactions show that selenious acid has a different constitution to sulphurous acid, being in fact a true dihydroxyl acid,  $\text{SeO}(\text{OH})_2$ .

The *ethoxylchloride*,  $\text{SeO}:\text{Cl}(\text{OEt})$ , is easily obtained by the action of alcohol on selenious chloride. T. C.

**Silicon Ethyl Series.** By C. FRIEDEL and A. LADENBURG (*Ann. Chim. Phys.* [5], 19, 390—406).—The authors refer to former papers on the organo-silicon compounds (*Ann. Chim. Phys.* [4], 9, 5; 19, 334; 23, 430; 27, 416—428).

In the present paper they give the results of attempts to prepare compounds containing as a nucleus 2 atoms of silicon  $\equiv\text{Si}-\text{Si}\equiv$ , and therefore analogous to ethane and its derivatives. The starting point for the preparation of these compounds is *silicon hexiodide*, which the authors have succeeded in preparing by heating silicon tetriodide with finely divided silver (reduced by zinc from moist silver chloride), in sealed tubes at  $290-300^\circ$  for several hours. The contents of the tube are freed from unaltered tetriodide by repeated washing with small portions of dry carbon bisulphide; a larger quantity of hot carbon bisulphide is then added, and the mixture filtered as rapidly as possible out of contact with the moisture of the air. On cooling, the solution deposits small colourless hexagonal prisms of  $\text{Si}_2\text{I}_6$ , which fume in moist air, and dissolve in potash with evolution of hydrogen. Silicon hexiodide may be fused in a vacuum, but partially decomposes at  $250^\circ$ . It cannot be distilled at atmospheric pressure or in a vacuum, but on heating a portion sublimes, and the remainder decomposes into the tetriodide and an orange substance which appears to be  $\text{SiI}_2$ .

*Silicon hexabromide*,  $\text{Si}_2\text{Br}_6$ , is obtained by adding an equivalent of bromine to a solution of the hexiodide in carbon bisulphide. It crystallises in rhombic plates, presenting the optical phenomena of biaxial crystals, and is therefore not isomorphous with the corresponding iodide.

*Silicon hexachloride*,  $\text{Si}_2\text{Cl}_6$ , is obtained by gently heating a mixture of silicon hexiodide and mercuric chloride. The product is distilled off, rectified over mercuric chloride, and purified by fractional distillation. It is a colourless liquid, distilling between  $144^\circ$  and  $148^\circ$ , and crystallising about  $-1^\circ$ ; it fumes in the air, and is decomposed by water, with formation of a product which in great part dissolves in the acid liquid. All attempts of the authors to prepare this substance in the dry way by the action of silicon, silver, zinc, sodium, and hydrogen on silicon tetrachloride at a high temperature, were unsuccessful. MM. Troost and Hautefeuille, however, have recently prepared  $\text{Si}_2\text{Cl}_6$  by the action of silicon tetrachloride on fused silicon, at a temperature at which porcelain begins to soften.

*Silico-oxalic hydrate*,  $\text{H}_2\text{Si}_2\text{O}_4$ .—When crystals of silicon hexabromide are introduced into ice water, hydrogen is evolved, and a white substance deposited which, after drying in a vacuum and then at  $100^\circ$ ,

has a composition expressed by the formula  $\text{H}_2\text{Si}_2\text{O}_4$ . Treated with potash, it gives off hydrogen in theoretical proportion, and when burnt with oxygen and heated in the air it decomposes with incandescence, leaving a residue of silica in the proportion required by the equation:  $\text{H}_2\text{Si}_2\text{O}_4 + \text{O} = \text{H}_2\text{O} + 2\text{SiO}_2$ . The air-dried substance contains 10·4 per cent. water, the formula  $\text{H}_2\text{Si}_2\text{O}_4 + 2\text{H}_2\text{O}$  requiring 12·8 per cent. The authors explain the formation of silico-oxalic hydrate by supposing  $\text{Si}_2(\text{HO})_6$  to be first produced, and to become  $\text{Si}_2\text{O}_2(\text{HO})_2$  by the loss of  $2\text{H}_2\text{O}$ . Although this substance is the chemical analogue of oxalic acid, it has no acid functions; bases, even the most dilute, decompose it with evolution of hydrogen, just as oxalic acid under certain conditions is decomposed by potash.

Silico-oxalic hydrate may also be prepared by the action of silicon hexiodide on absolute alcohol, the ethyl iodide, which is formed at the same time, being removed by distillation.

*Silicon hexethide*,  $\text{Si}_2(\text{C}_2\text{H}_5)_6$ .—Silicon hexiodide is added in small quantities to zinc ethyl in the proportion of  $\text{Si}_2\text{I}_6$  to  $3\text{ZnEt}_2$ . A brisk reaction ensues, and a white substance is deposited. The product is distilled, the distillate washed with water to remove zinc ethide, agitated with concentrated sulphuric acid (to remove a substance which appears to be oxide of silicon-triethyl), again washed with water, dried, and submitted to fractional distillation. The distillate boiling at  $150$ — $154^\circ$  is silicon tetrethide, that coming over between  $250^\circ$  and  $253^\circ$  is silicon hexethide,  $\text{Si}_2(\text{C}_2\text{H}_5)_6$ . Silicon hexethide is a limpid, slightly oily liquid, with a faint odour resembling that of silicon tetrethide. It burns with a bright flame, producing clouds of silica. Two vapour-density determinations, made at about  $300^\circ$ , gave the numbers 8·53 and 8·63, theory requiring 7·96. The excess was probably due to the presence of the above-mentioned oxide of silicon-triethyl. The density of the liquid silicon hexethide is 0·8510 at  $0^\circ$ , 0·8403 at  $20^\circ$ , compared with water at  $0^\circ$  and  $20^\circ$  respectively. This compound may be regarded as a derivative of silico-ethane,  $\text{Si}_2\text{H}_6$ , just as tetraphenylethane,  $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2$ , is a derivative of ethane.

J. M. H. M.

**Action of Certain Metals and Non-metals on Phosphorus Oxychloride.** The Existence of Leverrier's Phosphorus Suboxide. By B. REINITZER and H. GOLDSCHMIDT (*Ber.*, 13, 845—851).—When molecular silver is heated with phosphorus oxychloride in sealed tubes at  $250^\circ$ , the following bodies are formed: phosphorus trichloride and pentoxide, pyrophosphoryl chloride ( $\text{P}_2\text{O}_5\text{Cl}_4$ ), silver chloride, and silver ortho- and pyro-phosphates.

With metallic copper, phosphorus oxychloride yields cuprous chloride and phosphide, also phosphoric anhydride and pyrophosphoryl chloride. Under similar conditions, metallic mercury produces mercuric chloride, phosphide and phosphate, mercurous and phosphorous chlorides, pyrophosphoryl chloride, and a small quantity of phosphoric anhydride.

Sulphur and lead do not act on phosphorus oxychloride, and tin has no action on it at  $100^\circ$ . In addition to phosphorus trichloride, zinc metaphosphate and chloride, and small quantities of phosphoric anhydride and pyrophosphoryl chloride, metallic zinc forms phosphorus

suboxide,  $P_4O$ , described by Leverrier (*Ann.*, **27**, 167). This oxide, the existence of which was denied by Schrötter, is an orange-red powder, which reduces solutions containing silver, mercury, or gold, and when boiled with potash blackens and evolves phosphoretted hydrogen.

Magnesium and aluminium yield similar products to those obtained in the case of zinc. By the action of iron on the oxychloride, ferrous chloride and phosphate, and phosphorus trichloride and pentoxide are produced.

A modification of phosphorus suboxide,  $P_4O$ , appears to be formed by heating at  $250^\circ$  a mixture of phosphorus and the oxychloride,  $P_4 + POCl_3 = P_4O + PCl_5$ . It is a red substance, and differs from the ordinary modification inasmuch as it is not attacked by alkalis or by water, and does not reduce solutions of silver or gold.

With arsenic, phosphorus oxychloride yields the trichlorides of arsenic and phosphorus, also phosphoric anhydride and pyrophosphoryl chloride.

The authors consider that the results of these experiments are evidence in favour of the pentavalence of phosphorus, since isomeric oxychlorides of phosphorus were not produced in any instance.

W. C. W.

**Composition of Hydrated Barium Dioxide.** By E. SCHONE (*Ber.*, **13**, 803—807).—Only one hydrate of barium dioxide,  $BaO_2 \cdot 8H_2O$ , can be obtained between  $5^\circ$  and  $20^\circ$ , either by spontaneous decomposition of the compound  $BaO_2 \cdot H_2O$  under water, or by addition of a dilute solution of hydrogen peroxide to excess of barium hydrate.

G. T. A.

**Dissociation of Barium Dioxide.** By BOUSSINGAULT (*Ann. Chim. Phys.* [5], **19**, 464—472).—In this paper Boussingault narrates the series of attempts which he has made to devise a method of separating the oxygen of the atmosphere economically on an industrial scale. The method employed by him was the alternate peroxidation and reduction of baryta at a dull red and a bright red heat respectively. After a few heatings, it was found that the baryta almost loses its power of absorbing oxygen. The author demonstrated that this loss of activity is due to a change in the molecular state of the baryta induced by the high temperature required for the decomposition of barium dioxide under ordinary conditions. In fact, baryta obtained by very strongly heating the nitrate will scarcely take up oxygen, and even combines with water with extreme slowness. The experiments of Gay-Lussac on the decomposition of calcium carbonate by heat, and the subsequent researches of St. Claire Deville and Debray on dissociation, suggested to the author that in a vacuum the decomposition of barium dioxide might take place at a temperature low enough to have no injurious influence on the power of baryta to absorb oxygen. This was found to be the fact, barium dioxide dissociating at a low red heat in a vacuum, whereas it requires a bright red or orange heat under atmospheric pressure. The decomposition in a vacuum takes place at about the same temperature (the melting point of zinc,  $450^\circ C.$ ) as the absorption of oxygen by baryta under atmospheric pressure. At

a low red heat the power of baryta to absorb oxygen is not at all injured, and the alternate peroxidation and reduction may take place an indefinite number of times.

J. M. H. M.

**Crystalline Form of Magnesium.** By DES CLOIZEAUX (*Compt. rend.*, 90, 1101—1102).—The crystals obtained by Dumas by sublimation have the colour and lustre of silver, are malleable and sectile, but have no cleavage. The faces are often curved and the edges rounded. The usual form is a regular hexagonal prism, the basal planes of which are less brilliant than the lateral faces. The principal angle of the corresponding rhombohedron is  $80^{\circ} 3' 30''$ , and is therefore intermediate between that of zinc, the most acute of the rhombohedral metals, and arsenic.

C. H. B.

**The New Metals of Gadolinite and of Samarskite.** By M. DELAFONNAINE (*Compt. rend.* 90, 221—223).—Discoveries of ten rare earths have been announced by various chemists since the publication in 1878 of papers on terbium by Marignac and by the author. The latter believes that these alleged discoveries have really and definitely added to the list of elements only three new ones, viz., *ytterbium*, *decipium*, and *philippium*. *Samarium* is probably another real discovery, but further proofs are needed. *Mosandrum*, *holmium*, *thulium*, and the rest must be rejected, except possibly *scandium*, with which the author disclaims any acquaintance. Holmium is, according to the author, identical with philippium.

R. R.

**Vesbium and Norwegium.** By C. RAMMELSBERG (*Ber.*, 13, 250—251).—Scacchi (this vol., 445) has examined the green and yellow incrustations found in the clefts of Vesuvian lavas, and has obtained from them a red metallic acid, containing a new metal, vesbium. Its reactions closely resemble those of molybdenum.

Dahl (*Zeit. d. Geol. Gesellschaft*, 31, 480) claims to have discovered a new metal (norwegium) in the red nickel-pyrites of Kragerø (this Journal, 36, 890). The metal is white and not very malleable; sp. gr., 9.44. It dissolves in nitric acid with blue colour, which becomes green on dilution. Its salts give a green precipitate with alkalis, soluble in excess. Before the blowpipe it gives a yellow glass, becoming blue on cooling; with soda on charcoal, it gives a yellowish-green incrustation.

Ch. B.

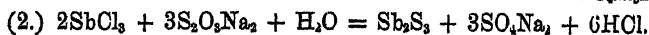
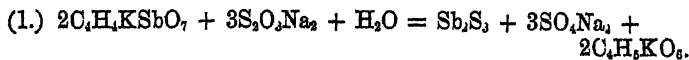
**Composition of Weldon-mud.** By J. POST and G. LUNGE (*Dingl. polyt. J.*, 236, 225—237).—In a paper recently published (*ibid.*, 235, 300) Lunge criticises Post's investigations as to the composition of Weldon-mud. In reply, Post gives a detailed account of his investigations which led him to affirm that it is erroneous to assume Weldon-mud to consist chiefly of a so-called calcium manganite ( $\text{MnO}_2$ ),  $\text{CaO}$ , since Weldon-mud itself, or when mixed even with an unusually large percentage of "base," contains but little lime ( $\text{CaO}$ ). It is further shown that at the present time in the Weldon process mud containing less than 0.5 of "base" to 1.0 of  $\text{MnO}_2$  is found. Lunge, in contradicting these statements, mentions that Post arrived

at his conclusions by analysing three or four samples of but "slightly washed," or "unwashed" mud; whereas the analyses of "well washed" mud and the conclusions drawn from the results seem to have been entirely ignored by Post. These contradictory statements have given rise to a large amount of correspondence between Lunge and Post, and the present paper gives a full account of the same. D. B.

**Borotungstates.** By D. KLEIN (*Bull. Soc. Chim.* [2], 33, 466—469).—*Potassium borodecitungstate*,  $2K_2O \cdot 12WO_3 \cdot B_2O_3 \cdot 15H_2O$ , is obtained in radiating masses, formed of acicular crystals, by boiling together for 12 hours equal weights of tungstic hydrate and potassium pentametaborate,  $K_2H_4B_5O_{10} \cdot 2H_2O$ . It is slightly soluble in cold, very soluble in hot water. At  $175^\circ$ , it loses all water of crystallisation, and if heated more strongly, a small quantity of boric acid is volatilised. In external appearance it resembles the metatungstate,  $K_2O \cdot 4WO_3 \cdot 5H_2O$ , but is much less soluble in water.

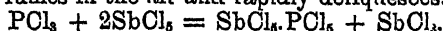
*Barium borodecitungstate*,  $2BaO \cdot 12WO_3 \cdot B_2O_3 \cdot 20H_2O$ , is obtained by adding a solution of 12 grams of barium chloride to a strong solution of 35 grams of the preceding compound. It forms large brilliant octohedrons, identical in appearance and crystalline form with those of the metatungstate, but more stable. At  $175^\circ$  they lose all water of crystallisation. The same compound is in all probability formed when barium chloride is added to the acidulated mother-liquors from the treatment of sodium tungstate, with an excess of boric acid. From this salt an acid was obtained, which, on concentration, crystallised in quadratic octohedrons, the angles of which were truncated by the faces of the primitive prism. C. H. B.

**Red Antimony.** By N. TÖDLU (*Dingl. polyt. J.*, 236, 336—340).—As the opinions concerning the composition of red antimony still differ in spite of the manifold investigations recently made, and several new text-books class it among the oxysulphides, and others among the trisulphides of antimony, the author thought it desirable to undertake a series of careful analyses of this compound, so as to enable him to decide this point, and also to determine whether the product prepared according to Wagner's method from tartar emetic differs in composition from that obtained from chloride of antimony. It was found that red antimony in both cases consists merely of antimony and sulphur, its composition being  $Sb_2S_3$ . Its formation by both methods may be illustrated by the following equations:—



The formation of sulphurous acid, which is invariably observed during the preparation of this compound, and the presence of free sulphur in the product after extraction with carbon bisulphide, point to the simultaneous result of a secondary process, which consists in the decomposition of sodium thiosulphate by means of tartaric or hydrochloric acid.

**Action of Antimony Pentachloride on Phosphorus Trichloride.** By H. KOHLER (*Ber.*, 13, 875—877).—When antimony pentachloride is slowly added to phosphorus trichloride, diluted with five times its bulk of chloroform, Weber's phosphorus antimony decachloride (*Pogg. Ann.*, 125, 78) is deposited as a white crystalline powder, which fumes in the air and rapidly deliquesces.



W. C. W.\*

## Mineralogical Chemistry.

**Crystal-tectonic of Silver.** By A. SADERBECK (*Jahrb. f. Min.*, 1879, 85—86).—Notwithstanding the limited number of known forms, silver exhibits great variety in its crystalline structure. There are three crystal types, viz., the octohedral, the cubical, and a subtype, the middle crystal. Twins according to the usual law of the regular system. The author observed in regard to the tectonic properties, a characteristic "shell-like structure," which is brought about by the union of subindividuals in the octohedral and cubical faces. Silver occurs also, like other precious metals, in "regular growths" (*regelmässigen Verwachsungen*), which are dependent on the arrangement of the crystals in certain directions, these directions being called by the author the tectonic axes. The tectonic axes are all the four kinds of crystallographical axes, viz., the fundamental axes, the prismatic axes, the diagonals of the octohedral faces and the rhombohedral axes. As a result of crystalline arrangement parallel to these directions, the various serrated, rod-like and wire-like forms may be cited. If the crystalline arrangement takes place parallel to various tectonic axes lying in one plane, this plane becomes the tectonic plane and plate-like formations are the final result.

In the case of native silver, cubical and octohedral faces appear as tectonic planes. The tectonic axes are not necessarily formed of similar axes, but can also be formed out of dissimilar axes. The primary and the prismatic axes appear as the tectonic axes in the cubical planes; in the octohedral planes the tectonic axes are the prismatic axes and the diagonals. Finally, the formation can take place parallel to various directions, resulting in skeleton growths. All the specimens of silver examined were embedded in calcite and accompanied by fluorspar and barytes: hence the author concludes that they were formed simultaneously in the wet way, more especially as the reticulated growth of the silver of Wittichen is intimately connected with the presence of barytes.

O. A. B.

**Artificial Production of Scorodite.** By VERNEUIL and BOURGEOIS (*Compt. rend.*, 90, 223—225).—To obtain scorodite, which is regarded as a hydrated ferric arsenate having the formula—





the authors heated iron wire in a sealed tube with a concentrated solution of arsenic acid at 150° for several days. At the end of the experiment the wire was found covered with fine crystals of scorodite of a bluish-green colour, and identical in form with those of native scorodite.

R. R.

**Felspar in the Basalt from the Hohen Hagen near Göttingen, and its Relation to the Felspar of Monte Gibeles in the Island of Pantellaria.** By C. KLEIN (*Jahrb. f. Min.*, 1879, 86—87).—Hausmann first described the felspar from Hohen Hagen in 1849, but Klein proved that the crystals were asymmetrical and not monosymmetrical. A careful optical examination showed the felspar to be oligoclase, and an analysis gave a further proof of the correctness of this conclusion, the result being as follows, viz. :—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaO. | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. |
|--------------------|----------------------------------|----------------------------------|------|------|-------------------|--------------------|
| 64.38              | 21.97                            | 0.45                             | 2.07 | 0.13 | 4.95              | 6.99 = 100.89      |

An optical examination of the Monte Gibeles felspar proved it to be identical with that from Hohen Hagen.

C. A. B.

**The Mica Group.** By C. RAMMELSBURG (*Ann. Phys. Chem.* [2], 9, 302—329).—This paper forms the second portion of the author's monograph on the chemical constitution of the micas (this vol., 224). The discussion of micas containing iron and magnesia is continued under several sections.

Micas corresponding with the general formula—



The specimens examined under this head are from Miask, Ilmengebirge; Filipstad, Sweden; New York; Greenland; Sterzing, Tyrol; Servance, the Vosges; Persberg, Sweden; and Brevig, Norway.

Another section comprising micas of the general formula— $M_4SiO_4.2R''_2SiO_4.R^vSi_3O_{12}$ , or  $M_2R''_2R^vSi_5O_{18}$ , includes specimens from Renschthal in the Black Forest; Lierwiese; Hitterö; Portland, Connecticut; and Radanthal; together with three varieties from Freiberg.

To certain specimens from Brevig in Norway, and from Wiborg, in Sweden, the general formula  $M_4SiO_4.3R''_2SiO_4.2R^vSi_3O_{12}$ , or  $M_2R''_2R^v_2Si_7O_{28}$ , is assigned.

The formula  $3M_4SiO_4.3R''_2SiO_4.4R^vSi_3O_{12}$ , or  $M_6R''_2R^v_4Si_9O_{36}$ , represents specimens from St. Dennis, in Cornwall, and from Persberg, in Sweden.

Micas of various composition, lithia-micas and baryta-micas, from specified sources, are then discussed under these respective heads.

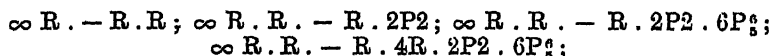
R. R.

**Crystallisation of Cyanite.** By M. BAUER (*Jahrb. f. Min.*, 1879, 84—85).—The results of Bauer's researches are briefly as follows, viz. :—(1.) Cyanite seldom exhibits an inclined laminated fracture (blätterbruch). (2.) From the angles observed between these in-

clined fracture-laminæ and certain faces (in conjunction with other angles), the axial relations were ascertained, viz., brachyaxis, macroaxis, vertical axis = 0.89912 : 1 : 0.69677. (3.) The twins parallel to M are recognised by the re-entering angles observed on T, and the differing position of the plane angle on M. (4.) The twins on which T exhibits re-entering angles and not P are formed occasionally by a revolution about the normal (in M) to the edge M : T, and not by a revolution about the edge M : P. (5.) Many twins occur according to the law, "the twin-axis the normal to M." (6.) Beer and Plucker first made it possible to distinguish the above-mentioned twins by means of their optical properties. (7.) The plane of the optical axes passes through the acute plane angles on M of 89° 45'. (8.) The twin-plane of the penetration-twins has the symbol  $-\frac{b}{2} : c$ . (9.) There are twins whose twin-plane is a face of P, and the twin-axis the normal to P. (10.) The last-mentioned twins are composite ones, parallel to M according to the second law given above, so that a further twin-law may be stated, viz., twin-plane a face of P, twin-axis a normal in P to the edge P : M. There were therefore six different penetration-twins observed. (11.) For each of the three twin-laws (having M as the twin-plane) there is a corresponding one where the individuals are twinned parallel to a face of P. One law is identical for P and M as twin-faces, and the number of twins parallel to P and M is therefore five in all. (12.) The twins parallel to P are not the original twins, but were brought about by the action of pressure, just as the twins of calcite according to the "first obtuser rhombohedron."

C. A. B.

**Caucasian Minerals.** By A. FRENZEL (*Jahrb. f. Min.*, 1878, 87—91).—*Rock-crystal from Kasbek.* Crystals mostly colourless and well developed, the combinations observed being—



dextrorotatory and lævorotatory. The crystals exhibit sometimes a rhombic or monosymmetrical appearance, and are occasionally covered with a soft black manganese ore or sometimes enclose chlorite.

*Heliotrope* is found as "pebble" in the valley of the Arpatschai, north of Alexandropol in Armenia; it has a fine dark leek-green colour, is free from the red iron oxide spots, has a sp. gr. of 2.12 to 2.27, and the following chemical composition, viz. :—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | FeO. | CaO. | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. | H <sub>2</sub> O. |
|--------------------|----------------------------------|------|------|------|-------------------|--------------------|-------------------|
| 88.90              | 0.71                             | 4.15 | 0.45 | 0.59 | 0.95              | 0.48               | 4.10 = 100.33     |

The basalts of Azkhur on the Upper Kur, between Borshom and Achalzich, contain fibrous *natrolite*, transparent and opaque crystals of *analcime* (2O2), transparent crystals of *apophyllite* (P. ∞P∞), also the variety of the same mineral called *ichthyophthalm*, in large foliated masses of a flesh-red colour.

*Magnetic-iron sand.*—This is found in very large quantity on the shores of the Caspian Sea, at various places near the Persian frontier,

more especially at Lenkoran. On Tscheleken, at various places, deposits of iron salts are found, which exhibit the following characteristics, viz. :—

1. A dirty ochre-yellow earthy mass constituting a series of mounds 6 meters high at Sarakaja, about  $1\frac{1}{2}$  kilometer from the west coast. The salt crops up to the surface, its colour increasing in intensity with the depth. The Turcomans call the salt "Karabuja," and use it for dyeing carpets. It is amorphous, and has the following composition :—

| SO <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaO.  | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. | H <sub>2</sub> O. | Residue (insol.). |
|-------------------|----------------------------------|-------|------|-------------------|--------------------|-------------------|-------------------|
| 30.30             | 19.00                            | 18.60 | 0.20 | 0.35              | 2.29               | 12.86             | 16.50 = 100.00    |

The insoluble residue was a calcareous marl.

2. Five kilometers north-east of Sarakaja, there is another iron salt deposit, the uppermost layer being ferrous sulphate about one foot in thickness, whilst underneath this layer there is a large one of a beautiful lemon to orange-yellow colour. The salt of the first layer has a fine green colour and often encloses wedge-shaped masses of iron pyrites. The composition of the green salt was

| SO <sub>3</sub> . | FeO.  | MgO. | H <sub>2</sub> O. |
|-------------------|-------|------|-------------------|
| 29.10             | 25.75 | 0.30 | 44.85 = 100.00    |

3. *Urusite* is the name which Frenzel assigns to the yellow salt above mentioned. Streak ochre-yellow. Sp. gr. 2.22. Hardness could not be determined. Occurs in nodules, earthy or pulverulent. On crushing a nodule very minute crystals are observed, which are rhombic, the forms being  $\infty P \infty$ .  $\infty P \infty$ .  $\infty P$ .  $P \infty$ .  $P$ .  $0P$ , but all the crystals do not exhibit these forms in combination,  $0P$  being occasionally absent, or sometimes it predominates at one end of the crystal and is extremely secondary at the other, thus giving a hemimorphous habit to the crystals. After deducting 3 per cent. of insoluble residue, urusite was found to have the following composition, viz. :—

| SO <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | Na <sub>2</sub> O. | H <sub>2</sub> O. |
|-------------------|----------------------------------|--------------------|-------------------|
| 42.08             | 21.28                            | 16.50              | 19.80 = 99.66     |

the formula deduced from this analysis being  $\text{Fe}_2\text{O}_3.2\text{Na}_2\text{O}.4\text{SO}_3 + 8\text{H}_2\text{O}$ .

4. North of Urus a salt occurs which resembles closely salt No. 1. The pulverulent masses enclose nodules of the salt, pieces of clay and fragments of gypsum. Sp. gr. 2.72. Chemical composition :—

| SO <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaO. | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. | H <sub>2</sub> O. | Residue (insol.). |
|-------------------|----------------------------------|------|------|-------------------|--------------------|-------------------|-------------------|
| 29.62             | 39.70                            | 4.70 | 0.20 | 0.74              | 3.28               | 10.96             | 10.80 = 100.00    |

C. A. B.

**New Minerals from the Andesite of Mount Arany.** By A. KocH (*Jahrb. f. Min.*, 1879, 83—84).—The author has already described the minerals (pseudo-brookite and szaboite) found in the above locality (*Jahrb. f. Min.*, 1878, 652), but he did not give an exact description of the rock in which they were found. He now states that the rock is an augite-andesite identical in character with the augite-andesite of Pachuca, in which G. v. Rath originally discovered tridy-

mite. Tridymite is present also in the augite-andesite of Mount Arany. Koch arrives at the following conclusion from his examination of the rock, viz., owing to the metamorphism exhibited, and the common occurrence of tridymite, it is highly probable that the original rock, after its solidification, was exposed to the action of fumaroles, resulting in the separation of silica and in making the molecules of the "ground-mass" more mobile, thus causing more complete crystallisation and a new formation of minerals. C. A. B.

**Ferruginous and Nitrated Mineral Waters.** By E. WILLM (*Bull. Soc. Chim.* [2], 33, 450—452).—These springs are situated in a valley of the Vosges between Saverne and Niederbronn, at Reipertswiller or Ripperville.

|   | Source<br>Spach. | Source<br>Cæsar. | Source<br>Madeleine. | Source<br>Arthur.                                    |
|---|------------------|------------------|----------------------|--|
| Carbonic anhydride (bicarbonates) ..... | 0.1552           | —                | —                    | —  |
| Carbonic anhydride (free) .....         | 0.1401           | —                | —                    | —  |
|   | or 70.9 c.c.     |                  |                      |  |
| Ferrous carbonate .....                 | 0.0968           | 0.0015           | 0.0009               | 0.0035   |
| Manganous „ .....                       | 0.0320           | 0.0006           | —                    | —  |
| Calcium „ .....                         | 0.0550           | 0.0592           | 0.0126               | 0.0159   |
| Magnesium „ .....                       | 0.0042           | 0.0107           | 0.0037               | 0.0039   |
| Ferric phosphate .....                  | 0.0096           | —                | —                    | —  |
| Potassium silicate .....                | 0.0113           | traces           | 0.0035               | } Almost exactly the same as the "source Madeleine." |
| Silica .....                            | 0.0087           | 0.0140           | 0.0076               |  |
| Potassium nitrate .....                 | 0.0130           | 0.1297           | 0.0051               |  |
| Calcium sulphate .....                  | 0.0044           | 0.0228           | 0.0119               |  |
| Magnesium „ .....                       | 0.0106           | 0.0043           | —                    |  |
| Potassium chloride .....                | 0.0528           | 0.0105           | 0.0203               |  |
| Sodium „ .....                          | 0.0326           | 0.0366           | 0.0117               |  |
| Magnesium „ .....                       | 0.0048           | 0.0228           | 0.0052               |  |
| Organic matter .....                    | 0.0155           | 0.0145           | 0.0081               |  |
|   | 0.3513           | 0.3572           | 0.0906               | 0.1070   |
| Solid matter found .....                | 0.3088           | 0.3568           | 0.0901               |  |

Potassium is present in much greater quantity than sodium; in the "source Cæsar" potassium nitrate constitutes one-third of the total solid residue. The deposit left by the "source Spach," dried at 120°, had the composition  $\text{SiO}_2$ , 24.75;  $\text{Fe}_2\text{O}_3$ , 56.62;  $\text{FePO}_4$ , 8.99;  $\text{CaCO}_3$ , 0.55;  $\text{MgCO}_3$ , 0.10;  $\text{H}_2\text{O}$ , 9.09. No manganese, arsenic, or organic matter was present. C. H. B.

## Organic Chemistry.

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**Vapour-tension of the Halogen Derivatives of Ethane.** By W. STAEDAL (*Ber.*, 13, 839--841).—The determination of the boiling points of the chlorine substitution-products of ethane, at pressures varying from 400 to 1060 mm., yields results which show that the increase of tension with the temperature depends not only on the molecular weight, but also on the constitution of the compounds. More heat is required to produce a given increase of tension in the symmetrical than in the unsymmetrical derivatives. A comparison of the bromine and chlorine substitution products shows that a bromine derivative has the same increase of tension for  $1^{\circ}$ , which is possessed by a compound containing, instead of 1 atom of bromine, 2 chlorine atoms attached to the same carbon atom, *e.g.*, ethyl bromide and ethylidene chloride, ethylidene chlorobromide and trichlorethane.

W. C. W.

**Preparation of Acetonitril.** By E. DEMARÇAY (*Bull. Soc. Chim.* [2], 33, 456—457).—When acetamide is distilled in a flask fitted with a Le Bel-Henninger tube the distillate consists at first of acetonitril, water, and ammonia, afterwards of acetonitril, water, and a small quantity of acetic acid. Apparently the acetamide, when heated a few degrees above its boiling point, splits up into acetonitril and water, and the latter decomposes a small quantity of acetamide, giving ammonia, which escapes, and acetic acid. When the quantity of acid in the liquid reaches a certain amount this secondary reaction ceases. This decomposition may be utilised for the preparation of acetonitril: acetamide, is mixed with a small quantity of glacial acetic acid, and boiled vigorously in a flask fitted with a Le Bel-Henninger tube having four or five bulbs. The distillate is dried over potassium carbonate. It is necessary to continue the boiling day and night for about a week, in order to decompose four or five hundred grains of acetamide, but the theoretical yield of the pure product is obtained. C. H. B.

**Pure Methyl Cyanide.** By A. GAUTIER (*Bull. Soc. Chim.* [2], 33, 515).—The author shows that the physical constants of methyl cyanide from the light hydrocarbons of coal, as given by Vincent and Delachanal (*ibid.* [2], 33, 407, this vol., 524) are almost identical with those he gave for acetonitril twelve years ago (*Ann. Chim. Phys.* [4], 17, 103), when he showed the identity of Pelouze's methyl cyanide and acetonitril. J. T.

**Note on Platinum Thiocyanate.** By G. WYROUBOFF (*Bull. Soc. Chim.* [2], 33, 402—403).—The compound which Marciano described as a new platinum thiocyanate (*ibid.*, 33, 250), and to which he assigned the formula  $\text{Pt}(\text{CNS})_3$ , is really potassium thiocyanoplatinate,  $\text{K}_3\text{Pt}(\text{CNS})_3$ , analysed some time ago by Buckton. The formula of the crystal is  $\text{K}_3\text{Pt}(\text{CNS})_3 + 2\text{H}_2\text{O}$ . Marciano's mistake arises from

relying on the estimation of water and metallic platinum. The supposed instance of octoatomic platinum therefore disappears.

J. M. H. M.

**Ethylene Iodopicate.** By L. W. ANDREWS (*Ber.*, 13, 244—245).—Ethylene iodide dissolved in chloroform acts at ordinary temperatures on finely powdered silver picrate. At 70—80° the action is rapid. The chloroform solution, freed from iodine by soda and dried, leaves on spontaneous evaporation ethylene iodopicate,  $C_6H_2(NO_2)_3O.C_2H_4I$ .

By crystallisation from alcohol, it is obtained in colourless needles (m. p. 69·5°), which become deep orange on exposure to light. It is insoluble in water, sparingly soluble in alcohol or ether, soluble in chloroform. Potassium cyanide gives with it a colouring-matter like picrocyanine, and alcoholic ammonia converts it into a sandy yellow crystalline substance, not yet examined.

Silver picrate (2 mols.), when heated with ethylene iodide (1 mol.) and chloroform at 100° for six hours, gave the above iodopicate, resinous matter, and a substance (m. p. 78°) easily soluble in alcohol. The latter is probably ethylene picrate, but has not yet been analysed.

Ch. B.

#### Carbohydrates from the Tubers of the Jerusalem Artichoke.

By E. DIMCK and B. TOLLENS (*Annalen*, 198, 228—255).—The tubers examined contained lævulin and a dextrorotary sugar, but little or no inulin.

The authors find that the body described by Kopp (*Annalen*, 156, 181) as a sugar and named synanthrose, of the assigned formula  $C_{12}H_{22}O_{11}$ , is really analogous to dextrin, and has the composition  $C_6H_{10}O_5$ ; they propose to name it lævulin. It is optically inactive, resembles the gums and dextrins in its properties, and enters into alcoholic fermentation with yeast. Boiled with very dilute hydrochloric acid, it gives a sugar which reduces Fehling's solution, and has a specific rotary power  $[\alpha]_D = -52\cdot7^\circ$ . Long heating with moderately dilute sulphuric acid, converts lævulin into lævulinic acid. The expressed juice of the tubers gives a fair yield of spirit on fermentation, the liquid also containing mannitol, glycerol, and, on one occasion, succinic acid.

W. R. H.

**Acetylation of some Carbohydrates by Liebermann's Process.** By A. HERZFELD (*Ber.*, 13, 265—268).—The acetyl in these compounds is best estimated by Schützenberger's method. Five grams of the body is heated in a Lintner's pressure flask at 120—140° with 20 c.c. of standard sulphuric acid (351 grams sulphuric acid of 1·831 sp. gr., = 75 per cent.  $SO_3$ , to 10 liters), and the solution titrated with potash. No blackening occurs, and the results are accurate. It has thus been found that Liebermann's process always yields the highest acetic derivatives.

*Octacetyl-glucose* has been described by Franchimont (*Ber.*, 12, 1940). The author finds for it the m. p. 134° instead of 100°. It reduces Fehling's solution.

*Octacetyl-lucose*,  $C_{18}H_{14}O_{11}Ac_8$ , is almost insoluble in ether, but crystallises from a mixture of alcohol and ethyl acetate; it is soluble in benzene and in acetic acid. It reduces Fehling's solution.

*Octacetyl-maltose*,  $C_{13}H_{14}O_{11}\bar{A}c_8$  (m. p.  $152^\circ$ ), resembles the dextrose compound, and crystallises in thin prisms.

*Octacetyl-saccharose* (m. p.  $78^\circ$ ) was obtained as a yellow resin, easily soluble in alcohol and ether. It does not reduce Fehling's solution; for which reason, amongst others, the author regards it as different from Schützenberger's octacetyl-diglucofucose.

*Acetyl-maltodextrin* (composition uncertain, m. p.  $98^\circ$ ) is more soluble than the maltose compounds, and is precipitated by water from its solution in alcohol and ethylic acetate in white flocks.

*Acetyl-erythro-dextrin* and *acetyl-achroo-dextrin*,  $C_6H_7(\bar{A}c)_3O_6$  (m. p. of both  $180^\circ$ ), require prolonged boiling for their production. They are insoluble in water (the sugar derivatives are somewhat soluble in hot water), acetic acid, alcohol and ether, but dissolve in a hot mixture of alcohol and ethylic acetate. From their solutions they separate as white powders; they do not reduce Fehling's solution. Ch. B.

**Saccharin.** By E. PELIGOT (*Compt. rend.*, 90, 1141—1143).—Saccharin (this vol., 232), whether obtained from glucose prepared from starch or from lævulose, is dextrorotatory. Its rotatory power, as determined by Laurent's polarimeter, is  $93.5^\circ$ ; that of ordinary sugar, under the same conditions, being  $67^\circ 18'$ . It is characterised by its relative stability, and may be volatilised almost without decomposition, does not ferment, and gives no reaction with Fehling's solution, even after prolonged boiling with dilute sulphuric acid. With potassium and calcium hydrates, it forms compounds analogous to the saccharates, and is converted by concentrated sulphuric acid into a substance analogous to sulphosaccharic acid. When acted on by potassium permanganate, it is slowly converted into water and potassium carbonate, part of the manganese being precipitated as hydrated dioxide. One gram of saccharin requires 4.6 grams of crystallised permanganate for complete oxidation. Nitric acid is without action unless highly concentrated, and it may therefore be purified by treatment with this acid properly diluted. Saccharin is more readily obtained from calcium lævulosate than from inverted sugar or starch glucose. It will probably be found in many commercial saccharine products, and its presence will serve to explain the anomalous results sometimes obtained with the saccharimeter. C. II. B.

**Vapour-density of the Viscous Polymeride of Isobutaldehyde.** By F. URSCH (*Ber.*, 13, 590—594).—The vapour-density of the viscous modification of isobutaldehyde (obtained by the action of potassium carbonate on ordinary isobutaldehyde), as determined by Naumann's method (viz., by distillation with aqueous vapour), is 211, the calculated for  $(C_4H_8O)_3 = 216$ , whilst by Hofmann's method the number 88.88 was obtained,  $C_4H_8O = 72$ . This shows that the molecule  $(C_4H_8O)_3$  undergoes dissociation on conversion into the gaseous state, even under diminished pressure. T. C.

**Derivatives of Isobutaldehyde.** By A. LIPP (*Ber.*, 13, 905—908).—When ammonia gas is passed into an ethereal solution of isobutaldehyde, a compound having the composition  $C_{23}H_{42}ON_6$  is pro-

duced, thus:  $7\text{C}_4\text{H}_8\text{O} + 6\text{NH}_3 = (\text{C}_4\text{H}_8)_6\text{ON}_6\text{H}_6 + 6\text{H}_2\text{O}$ . This substance, which can also be prepared by pouring the aldehyde into an excess of strong ammonia, forms glistening crystals belonging to the hexagonal system. It melts at  $31^\circ$  and evolves ammonia at  $90^\circ$ ; at a higher temperature it yields a colourless liquid, having the composition  $\text{C}_4\text{H}_{16}\text{N}$ .

By the action of a 30 per cent. solution of hydrocyanic acid on the ammonia compound, amidoisovaleronitril and hydroxyisovaleronitril are produced:  $(\text{C}_4\text{H}_8)_6\text{ON}_6\text{H}_6 + 7\text{HCN} = 6\text{C}_4\text{H}_8(\text{NH}_2).\text{CN} + \text{C}_4\text{H}_8(\text{OH}).\text{CN}$ . Imidoisovaleronitril is formed at the same time by the decomposition of the amidonitril. The crude product of the reaction is treated with a 5 per cent. solution of hydrochloric acid and extracted with ether, which removes the imidovaleronitril and the hydroxynitril. After the addition of ammonia to the residue, the amidoisovaleronitril can be extracted with ether.

The ethereal solution is dried over calcium chloride and saturated with dry hydrochloric acid gas, when amidoisovaleronitril hydrochloride is deposited. The salt is very soluble in water and in absolute alcohol. The free base is a yellow alkaline liquid, which splits up at the ordinary temperature into ammonia and imidoisovaleronitril. The latter compound can be separated from hydroxyisovaleronitril by the insolubility of its hydrochloride in absolute ether. The hydrochloride is decomposed by water.

By the action of ammonia on this salt, two isomeric imidonitrils are formed, viz., a crystalline solid and an oily liquid.

Hydroxyisovaleronitril can be prepared by the direct union of isobutaldehyde with dry hydrocyanic acid. It is a colourless oily liquid, soluble in alcohol and ether. It is decomposed by heat into hydrocyanic acid and the aldehyde. W. C. W.

**Glyoxylic Acid.** By C. BÜTTINGER (*Annalen*, 198, 203).—After giving a short historical sketch of the work done on the subject by Debus, Church, Perkin, Duppa, and others, the author proceeds to describe his own experiments. The glyoxylic acid used was prepared by Debus's method.

A white pulverulent basic calcium salt was obtained by adding lime water to a cold saturated solution of calcium glyoxylate, and this basic salt is looked upon as the intermediate substance, from which calcium glycolate and oxalate are formed on *boiling*, as observed by Debus. The normal calcium salt crystallised from cold dilute solutions was found to contain  $4\text{H}_2\text{O}$ ; that crystallised from hot concentrated solutions,  $3\text{H}_2\text{O}$ .

On treating syrupy glyoxylic acid with hydrocyanic acid and a small quantity of hydrochloric acid, glycollic, formic, and carbonic acids were formed, together with ammonium chloride. The formation of a double salt of calcium glycolate and oxalate was observed. No oxalic acid was produced.

Sulphuretted hydrogen is readily absorbed by glyoxylic acid. On exposure to the air for some days, a readily soluble crystalline substance was formed, to which the author assigns the formula  $\text{C}_4\text{H}_4\text{SO}_6$ , as probable, although the analytical numbers do not agree with it.



From the uncrystallisable residue, the calcium salts of two acids containing sulphur were obtained, one of them being perhaps that of thiodiglycollic acid,  $C_4H_4SO_4Ca$ , the other yielding an uncrystallisable calcium salt. By the action of sulphuretted hydrogen in presence of silver oxide, there were formed sulphoglycollic acid, sulphodiglycollic acid, and a sulphuretted oil of the formula  $n(C_2H_3S_2O)$ . Oxalic acid is formed at the same time in relatively large quantity.

By the action of alcoholic ammonia on an alcoholic solution of glyoxylic acid, a white pulverulent precipitate, ammonium amidoglyoxylate, was thrown down, the temperature being kept low during the reaction. On boiling the aqueous solution, ammonia and carbonic anhydride escape, and when the dark-coloured solution is evaporated, a syrupy liquid is left, probably a condensation-product containing five carbon atoms in the molecule. The residual alcohol solution from the ammonium amidoglyoxylate, when left exposed to the air, deposited a dark powder, which proved to be a fine red colouring-matter; its analysis did not lead to decisive results.

Aniline acts very energetically on glyoxylic acid, giving a precipitate at first yellow, afterwards becoming deep yellowish-red. The residue exhausted with ether alcohol is insoluble in water, slightly soluble in alcohol, the solution dyeing silk of a pure yellow colour. It is a mixture. By treatment with barium hydrate, a barium salt was obtained, aniline being separated. It is in all probability barium aniloglyoxylate. By boiling the original crude substance with water, a residue was left, consisting of the anhydride of the acid. Boiled with barium hydrate, it yielded the impure barium salt.

The crude substance formed by the action of aniline on glyoxylic acid, when distilled from a small retort, gave a crystalline sublimate of carbanilide, together with aniline, carbonic oxide, carbonic anhydride, water, and coloured vapours.

The author, in conclusion, sums up his results as follows:—

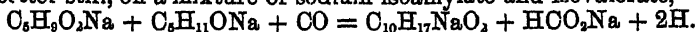
- (1.) The transformation of glyoxylic acid into glycollic and oxalic acids depends on the decomposition of a salt of definite composition.
- (2.) With hydrocyanic acid and sulphuretted hydrogen, it behaves similarly to its homologue, pyruvic acid.
- (3.) Ammonia converts glyoxylic acid into amidoglyoxylic acid; aniline into aniloglyoxylic acid.
- (4.) Glyoxylic acid behaves like an aldehyde.
- (5.) Glyoxylic acid is sharply distinguished from pyruvic acid by its slighter tendency to condensation, which is explained by the absence of a hydrocarbon radicle (methyl).

W. R. H.

**New Synthesis of Carbon Acids.** By A. GEMFNER, in conjunction with O. FRÖLICH and A. LOOSS (*Annalen*, 202, 288—331).—Berthelot has shown (*Compt. rend.*, 41, 955) that formic acid can be synthesised by the action of carbonic oxide on sodium hydrate, and later (*Ann. Chim. Phys.* [3], 61, 463) that propionic acid can be obtained, although in very small quantity, by the action of carbonic oxide on sodium ethylate in alcoholic solution at temperatures below  $100^\circ$ , a result confirmed by Hagemann (*Ber.*, 4, 877; this Journal, 1872, 143). The author has reinvestigated the subject, employing

dry metallic alcoholates, and higher temperatures. Sodium ethylate heated to  $190^\circ$  in a current of carbonic oxide yielded (in addition to the formate invariably obtained in all these reactions) sodium propionate, and also a considerable quantity of acetate; the latter was probably formed by a secondary reaction,  $C_2H_5NaO + 2NaOH = C_2H_3O_2Na + Na_2O + 4H$ , induced by the high temperature: an experiment at  $160^\circ$  confirmed this view, the proportion of acetate being much reduced.

Sodium methylate heated at  $160^\circ$  in carbonic oxide yielded acetate in small quantity. Sodium isoamylate heated with carbonic oxide at  $210^\circ$  gave no caproate, but the salts of formic and isovaleric acids, and of a new acid,  $C_{10}H_{18}O_2$ . Further experiments made to elucidate the formation of this acid showed that the necessary conditions were the action of carbonic oxide on a mixture of sodium isoamylate and hydrate,  $2C_5H_{11}ONa + 2NaOH + CO = C_{10}H_{17}NaO_2 + CHNaO_2 + Na_2O + 6H$ ; or better still, on a mixture of sodium isoamylate and isovalerate,



The pure acid,  $C_{10}H_{18}O_2$ , is an oil of peculiar odour, of sp. gr. 0.961 at  $12^\circ$ : it boils at  $268-270^\circ$ , and is probably amenylovaleric acid,  $C_4H_5(C_6H_5).COOH$ . There are formed at the same time diamenylovaleric acid,  $C_4H_7(C_6H_5)_2.COOH$  (b. p.  $300-306^\circ$ ); a ketone (b. p.  $208-209^\circ$ ) of quince-like odour, and sp. gr. 0.845 at  $12^\circ$ , probably amylovalerone,  $C_{14}H_{28}O$ , and another liquid boiling between  $279^\circ$  and  $285^\circ$ , possibly butenylbutylvalerone,  $C_{17}H_{32}O$ .

A mixture of sodium ethylate and hydrate heated in carbonic oxide at  $205^\circ$  yielded salts of the following acids, normal butyric, diethylacetic, triethenylbutyric ( $C_{10}H_{14}O_2 = C_3H_4(C_2H_3)_3.COOH$ , distilling between  $240-260^\circ$ ) and mesitylenic, and also the following ketones: propyl diethylketone,  $C_3H_7.CO.CHEt_2$ , boiling between  $180-190^\circ$ , and  $C_{15}H_{24}O_2$ , boiling between  $280^\circ$  and  $300^\circ$ , probably



Sodium methylate and acetate heated in carbonic oxide at  $200^\circ$  gave salts of propionic acid, and of an acid which is probably tetra- or penta-methylated propionic acid. Sodium ethylate and isovalerate under like conditions gave a salt of methylpropylpropionic acid,  $CPrMeH.CH_2.COOH$  (b. p.  $220^\circ$ ), differing from Grimshaw's isocentanthylic acid (b. p.  $210-213^\circ$  *Annalen*, 166, 168; this *Journal*, 1873, 314), whilst its formation from an isovalerate precludes the possibility of its being normal cenanthylic acid (b. p.  $223-224^\circ$ ). The other acids obtained were ethyl-diethenylisovaleric acid,  $C_8H_7Et(C_2H_3)_2O_2$ , distilling between  $270^\circ$  and  $280^\circ$ ,  $C_{13}H_{20}O_2$ , probably ethyltriethenylisovaleric acid, distilling between  $280^\circ$  and  $300^\circ$ , and a thick oily liquid distilling above  $360^\circ$ , of the formula  $C_{23}H_{30}O_2$  (?), probably ethyloctaethenylisovaleric acid, also a small quantity of a solid acid, apparently mesitylenic. The ketones obtained in this reaction were, ethylisobutylketone,  $Et.CO.CH_2.CHMe_2$  (b. p.  $132-134^\circ$ );  $C_{15}H_{20}O$ , boiling at  $163-168^\circ$ ;  $C_{25}H_{42}O$  or  $C_{23}H_{40}O$ , distilling between  $200^\circ$  and  $210^\circ$ ;  $C_{27}H_{46}O$  or  $C_{27}H_{44}O$ , distilling between  $240^\circ$  and  $260^\circ$ .

A mixture of sodium acetate and ethylate heated with zinc-dust to

240—250°, gave the same acids as were obtained on heating acetate and ethylate in carbonic oxide.

Sodium ethylate and hydrate heated at 160° in carbonic oxide gave scarcely any ketones, a small quantity of butyrate, and much formate. Sodium hydrate heated in carbonic oxide at 160° gave a very large yield of formate,\* and a small quantity of the salt of an acid richer in carbon; heated in a mixture of carbonic oxide and ethylene, it gave in addition to formate, a small quantity of a salt, whose sodium contents was intermediate between that of acetate and propionate.

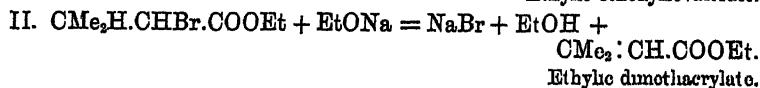
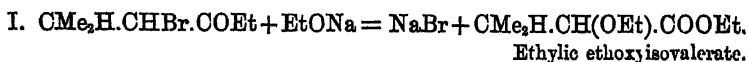
Sodium phenylate did not react with carbonic oxide, nor sodium isovalerate either with carbonic oxide or zinc-dust. A. J. G.

### Compound of Titanium Tetrachloride with Acetic Chloride.

By A. BERTRAND (*Bull. Soc. Chim.* [2], 33, 403—405).—On mixing titanium chloride with acetic chloride a precipitate is formed of yellow octohedral crystals, soluble in excess of acetic chloride. The crystals are rapidly decomposed by moist air, giving off thick fumes of hydrochloric acid; they are permanent in dry air and in dry hydrochloric acid gas; they melt at 25—30°, and recrystallise on cooling. Distillation at atmospheric pressure resolves them into titanium tetrachloride and acetic chloride. Carbon bisulphide dissolves them. The results of analysis agree with the formula  $C_2H_4OCl.TiCl_4$ .

J. M. H. M.

**New Mode of Forming Dimethacrylic Acid.** By E. DUVILLIER (*Ann. Chim. Phys.* [5], 19, 428—432).—When ethyl bromisovalerate is treated with a solution of sodium ethylate in absolute alcohol, the following reactions occur simultaneously:—

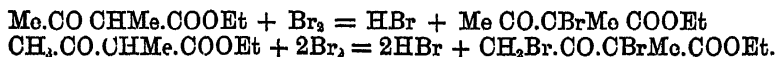


After boiling for several hours with inverted condenser, the alcohol is distilled off, water added to the residue, the supernatant liquid separated, dried, and distilled. The distillate passing over between 155° and 190° is saponified with alcoholic potash; the alcohol removed by distillation; excess of potash exactly neutralised by sulphuric acid; the potash salts converted into zinc salts by means of zinc sulphate; and the solution evaporated to dryness on the water-bath. The residue is treated with alcohol; sulphuric acid added to the alcoholic solution to remove the zinc; the free acids dissolved by shaking with ether; and the ethereal solution evaporated;—when dimethacrylic acid separates in colourless transparent crystals, but slightly soluble in water, very soluble in alcohol and ether. This dimethacrylic acid is identical with the acid obtained by Neubauer by oxidising the valeric acid from fermentation amyl alcohol (*Annalen*, 106, 63), and the acid obtained by Miller by oxidising isobutylformic acid from isobutyl cyanide (*Ber.*, 11, 1526, 2216). Its formation by the reaction de-

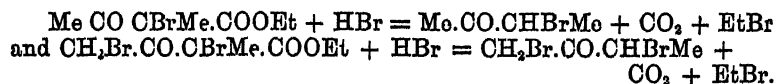
\* Comp. Merz and Tihirica (*Ber.*, 13, 23; this Journal, Abstr., 1880, 874).

scribed in this paper is analogous to the formation of crotonic acid by the action of alcoholic potash on ethyl bromobutyrate (Hell and Lauber). Dimethacrylic acid can now be prepared by three completely different synthetical methods, including that of Semiatzin and Saytzeff (*Annalen*, 185, 157). J. M. II. M.

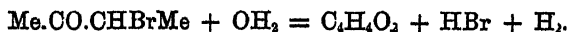
**Tetrolic and Oxytetrolic Acids and their Homologues.** By E. DEMARÇAY (*Bull. Soc. Chim.* [2], 33, 516—525)—Ethylic methylacetoacetate, when acted on by bromine, gives the following reactions, according to the amount of bromine employed:—



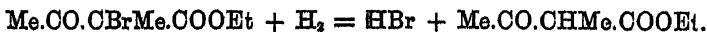
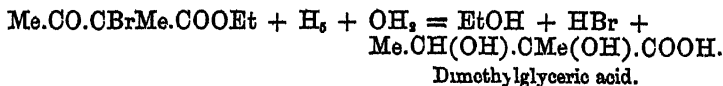
If the crude products are allowed to stand for some time, the hydrobromic acid present gives rise to the reactions—



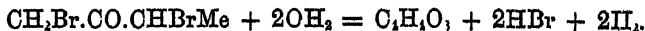
But if the products be treated at the proper time with alcoholic potash, the following reaction takes place:—



Other hydrogenised products corresponding with the hydrated compound,  $3\text{C}_4\text{H}_4\text{O}_2 + \text{H}_2\text{O}$ , are formed simultaneously according to the following reactions:—



But the methylacetoacetic acid thus regenerated is decomposed by alcoholic potash, giving rise to known products. From these equations it is seen that a third only of the brominated ether has to be decomposed by hydrobromic acid. The dibrominated product under the action of alcoholic potash gives analogous reactions—



Other acids are produced, some similar to those formed in the previous reactions, but they have not yet been sufficiently examined.

In the case of the homologous acetoacetic ethers, the reactions are parallel at all points. The author has studied the ethyl salts of methyl-, ethyl-, propyl-, isopropyl-, isobutyl-, and methylethyl-acetoacetic acid.

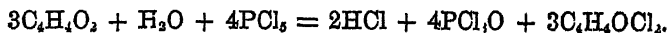
Tetrolic acid is obtained as follows:—

Ethylic methylacetoacetate with a little water is treated with bromine added in small portions, the flask being kept cool (about 15°), until a nearly equal molecular quantity of bromine has been added. After allowing the liquid to stand for ten to eleven hours at 20°, two

to three times its volume of water is added, when a heavy oil separates out. To this oil alcoholic potash is gradually added, the flask being kept cool. Afterwards the alcohol is removed by a current of steam; acetone and other products going over at the same time. The acids retained by the potash are set free by a slight excess of hydrochloric acid. On cooling, much of the tetrolic acid separates out; the rest is removed by agitation with ether. In the case of the higher homologues of tetrolic acid, after the addition of hydrochloric acid, the liquid is distilled with 5—6 volumes of water until nothing but water passes over. The acids are then extracted by means of ether. Oxy-tetrolic acid and its homologues are prepared like the preceding.

Tetrolic acid is a white solid, crystallising in triclinic prisms (m. p.  $189^{\circ}$ ), boiling with decomposition at about  $260$ — $280^{\circ}$ . Heated in an inert gas, it sublimes. Very soluble in boiling water, in alcohol, and in ether. At  $18.5^{\circ}$ , one of acid dissolves in 65.7 parts of water. Scarcely soluble in chloroform, cold or hot, but soluble in boiling chloroform in presence of a little alcohol. Odour faint, like that of propionic acid. Taste and reactions acid; and its salts crystallise readily.

Three types of salts are formed, one represented by the copper salt,  $\text{CuO} \cdot \text{C}_4\text{H}_4\text{O}_5$ , a second by the barium salt,  $\text{BaO} \cdot 2\text{C}_4\text{H}_4\text{O}_5$ , and the third and most common one,  $2\text{M}_2\text{O} \cdot 5\text{C}_4\text{H}_4\text{O}_5$ . Anhydrous salts of ammonium, silver, copper, potassium, and sodium, and hydrated salts of barium, calcium, magnesium, and zinc are described. Ferric chloride gives with the ammonium salt a violet to bright rose-coloured precipitate. The acid and all its homologues are coloured an intense violet-red by ferric chloride. Heated at  $150^{\circ}$  with water for some time, there is no change. With dilute hydrochloric acid at the same temperature, a black resin is produced with the odour of crotonic aldehyde. Heated to the same temperature, or even lower, with potash and a little water it yields formic and propionic acids,  $\text{C}_4\text{H}_4\text{O}_5 + 2\text{H}_2\text{O} = \text{CH}_2\text{O}_2 + \text{C}_3\text{H}_5\text{O}_2$ . Bromine yields an oily body which easily decomposes. Nitric acid oxidises the acid completely, yielding small crops of crystallised nitro-compounds, which may or may not be soluble in ether with a beautiful blue colour. Potassium permanganate gives acetic acid and carbonic anhydride. Sodium-amalgam, and zinc with acid appear to have no action. Phosphorus pentachloride attacks the acid slowly in the cold as follows:—



On washing well with water, the last compound is obtained as a colourless oil boiling at  $172^{\circ}$  without change, unless boiled for a long time; its sp. gr. at  $10.5^{\circ}$  is 1.471. It is not sensibly attacked by alcohol at  $150^{\circ}$ , or by water, potash, or ammonia at  $100^{\circ}$ . With chlorine, this compound forms  $\text{C}_4\text{H}_4\text{Cl}_4\text{O}$ , a beautifully crystallised body, m. p.  $49^{\circ}$ , which gradually decomposes; with bromine this gives  $\text{C}_4\text{H}_4\text{Cl}_2\text{Br}_2\text{O}$ , which fuses at  $66^{\circ}$  and gives off bromine and hydrobromic acid.

J. T.

**Hydroxyacrylic Acid.** By P. MELIKOFF (*Ber.*, 13, 271—274).—When alcoholic potash is gradually added to a solution of monochlorolactic acid (prepared by direct addition of hypochlorous acid to acrylic acid, *Ber.*, 12, 2227), the mixture being kept cool, potassium chloride

is formed together with the potassium salt of hydroxyacrylic acid,  $C_3H_3KO_3 \cdot 1\frac{1}{2}H_2O$ . This potassium salt separates after the chloride in globular or reniform groups of needles, which may be crystallised from hot alcohol, but decompose at  $80^\circ$ . By double decomposition it yields a silver salt,  $C_3H_3AgO_3$ , which decomposes at  $100^\circ$ . The free acid may be obtained by adding sulphuric acid to a solution of the potash salt and shaking with ether. It is a volatile transparent and rather mobile liquid, the vapour of which is highly irritating. Neither the acid nor its salts gives a red colour with ferrous sulphate, as pyrrocemic acid does. When a solution of the calcium salt (obtained by neutralising the free acid with calcium carbonate and precipitating with alcohol) is heated on the water-bath, water is assimilated and calcium glycerate,  $C_3H_5CaO_4 \cdot H_2O$ , is formed. Glyceric acid is likewise produced by boiling an aqueous solution of the silver salt of liquid monochlorolactic acid.

A mixture of hydroxyacrylic acid with fuming hydrochloric acid becomes very hot, and on agitation with ether yields solid chlorolactic acid (m. p.  $78-79^\circ$ ), crystallising in silky feathery needles. This is identical with the acid prepared by Richter (*J. pr. Chem.*, 20, 193), by oxidising epichlorhydrin with nitric acid. It is not attacked by fuming hydrochloric acid. On the other hand, monochlorolactic acid from acrylic acid is liquid, and when heated at  $100^\circ$  with highly concentrated hydrochloric acid, yields dichloropropionic acid (m. p.  $50^\circ$ ).  
Ch. B.

**Carbonyl Bromide.** By A. EMMERLING (*Ber.*, 13, 873—875).—Impure carbonyl bromide can be obtained in small quantities by gently warming a mixture of sulphuric acid (50 parts), potassium chromate (20—25 parts), and bromoform (5 to 10 parts). The operation is conducted in a flask provided with an upright condenser to which a U-tube, surrounded by a freezing mixture, is attached. After the free bromine has been removed from the crude product by slow distillation over metallic antimony, the carbonyl bromide is obtained as a colourless heavy liquid boiling between  $12^\circ$  and  $30^\circ$ .  
W. C. W.

**Syntheses by means of Ethyl Malonate.** By M. CONRAD and C. A. BISCHOFF (*Ber.*, 13, 595—601).—A continuation of the authors' previous work on this subject (this Journal, 36, 707 and 918), and for the general methods of preparation of many of the following compounds, the earlier communications must be consulted.

*Ethyl isopropylmalonate*,  $CHMe_2 \cdot CH(COOEt)_2$ , is a colourless liquid (b. p. =  $213^\circ$ ); its sp. gr. is 0.997 at  $20^\circ$  compared with water at  $15^\circ$ .

*Isopropylmalonic acid*,  $CHMe_2 \cdot CH(COOH)_2$ , crystallises in prisms (m. p. =  $83^\circ$ ) which decompose at  $175-180^\circ$  into carbonic anhydride and isopropylacetic acid,  $C_6H_{10}O_2$  (b. p. =  $174^\circ$ ), identical with the valerianic acid obtained by Erlenmeyer and Hell (*Annalen*, 160, 264) from isobutyl cyanide.

*Ethyl ethylmethylmalonate*,  $CMeEt(COOEt)_2$ , (b. p. =  $207^\circ$ ); sp. gr. = 0.994 at  $15^\circ$ .

*Ethylmethylmalonic acid*,  $CMeEt(COOH)_2$ , crystallises in prisms

(m. p. =  $118^{\circ}$ ) which decompose on heating into carbonic anhydride and ethylmethylacetic acid,  $C_5H_{10}O_2$ , which is an optically inactive liquid (b. p. =  $173^{\circ}$ ), and is identical with the ethylmethylacetic acid obtained by Saur (*Annalen*, 188, 257) from ethyl acetoacetate, and with that obtained by Schmidt and Berendes (*Annalen*, 191, 117) by heating tiglic acid with hydriodic acid, and with that prepared by Pagenstecher (*Annalen*, 195, 121) from bromhydrotiglic acid by the action of sodium-amalgam, and also with the product obtained by Böcking (Inauguraldiss.: Würzburg, 1879) by the action of hydriodic acid on ethomethoxalic acid. A determination of the solubility of the silver salt of this acid shows that the valerianic acid obtained from commercial amylenes is not ethylmethylacetic acid, as stated by Eltekoff (*Ber.*, 10, 706). The authors confirm Erlenmeyer's supposition that the optically active valerianic acid from active amyl alcohol is either a molecular compound or a mixture of isopropyl- and ethylmethyl acetic acid.

*Ethyl isobutylmalonate*,  $C_4H_9.CH(COOEt)_2$  (b. p. =  $225^{\circ}$ , sp. gr. = 0.983 at  $15^{\circ}$ ).

*Ethyl dioctylmalonate*,  $C(C_8H_{17})_2(COOEt)_2$ , from octyl iodide (b. p.  $221^{\circ}$ ), is a colourless oil (b. p. =  $338^{\circ}$ ); its sp. gr. is 0.896 at  $18^{\circ}$  compared with water at  $15^{\circ}$ .

*Dioctylmalonic acid*,  $C_{18}H_{36}O_4$ , forms colourless crystals (m. p.  $75^{\circ}$ ) which are insoluble in water.

*Dioctylacetic acid*,  $C_{18}H_{36}O_2$ , is a white crystalline mass (m. p. =  $39^{\circ}$ , b. p. =  $300^{\circ}$ ), which is identical with an isostearic acid obtained by Gutzeit from ethyldioctylacetoacetic acid.

*Ethyl allylmalonate*,  $C_3H_5.CH(COOEt)_2$ , b. p. =  $220^{\circ}$ ; sp. gr. = 1.018 at  $16^{\circ}$  (water at  $15^{\circ}$  = 1).

*Allylmalonic acid*,  $C_5H_8O_4$  (m. p. =  $103^{\circ}$ ), belongs to the fumaric series, and is isomeric with hydromucic acid. Allylacetic acid,  $C_5H_8O_2$  (b. p.  $184^{\circ}$ ), is identical with the acid obtained by Zeidler (*Annalen*, 187, 30) from ethylacetoacetic acid.

*Ethyl diallylmalonate*,  $C(C_3H_5)_2(COOEt)_2$ , b. p. =  $240^{\circ}$ ; sp. gr. = 0.996 at  $14^{\circ}$  (water at  $15^{\circ}$  = 1).

*Diallylmalonic acid*,  $C_5H_{10}O_4$ , crystallises in prisms (m. p.  $133^{\circ}$ ). *Diallylacetic acid*,  $C_5H_{10}O_2$  (b. p. =  $219^{\circ}$ ), from the preceding, is identical with that described by Wolff (*Ber.*, 10, 1956) and Reboul (*Compt. rend.*, 84, 1233).

*Ethyl benzylmethylmalonate*,  $CH_2Ph.CMe(COOEt)_2$ , (b. p. =  $300^{\circ}$ ); sp. gr. = 1.064 at  $19^{\circ}$  (water at  $15^{\circ}$  = 1). This acid can also be obtained by the action of methyl iodide on ethyl benzylsodiummalonate, or by the action of benzoic chloride on ethyl methylsodiummalonate.

*Benzylmethylmalonic acid*,  $C_{11}H_{14}O_4$ , consists of crystals, m. p. =  $135^{\circ}$ .

*Benzylmethylacetic acid*,  $C_{10}H_{12}O_2$  (m. p. =  $37^{\circ}$ , b. p. =  $272^{\circ}$ ), is identical with the substituted acetic acid obtained from ethyl benzylmethylacetoacetate (*Ber.*, 11, 1056), also with the phenylbutyric acid obtained by the addition of hydrogen to the phenylcrotonic acid, prepared according to Perkin (this Journal, 31, 391) from benzaldehyde and propionic anhydride, and also with that produced by the addition of

hydrogen to the acid (*Annalen*, 193, 810) obtained by the action of sodium on benzyl propionate.

*Ethyl nitrosomalonnate*,  $\text{CH}(\text{NO})(\text{COOEt})_2$ , is obtained by the action of nitrous acid on an alcoholic solution of ethyl sodium malonnate. It is a yellow oil which is decomposed on distillation; sp. gr. = 1.149 at  $15^\circ$ .

*Nitrosomalonic acid*,  $\text{C}_3\text{H}_3\text{NO}_3$ , is obtained from the silver salt, and is identical with the acid described by Baeyer (*Annalen*, 131, 292). A crystalline *potassium salt*,  $\text{C}_3\text{HNO}_3\text{K}_2 + \frac{1}{2}\text{H}_2\text{O}$ , was prepared. On distillation, this acid splits up into carbonic anhydride, water, and hydrocyanic acid.

*Ethyl nitrosobenzylmalonnate*,  $\text{C}_7\text{H}_7\text{C}(\text{NO})(\text{COOEt})_2$ , is obtained by the action of sodium ethylate and benzyl chloride on ethyl nitrosomalonnate. On saponification with potash, it gives a crystalline potassium salt which, on dry distillation, splits up into potassium cyanide and carbonate and benzyl alcohol. The free acid undergoes a similar decomposition on boiling with water.

*Ethyl monochloromalonnate*,  $\text{CHCl}(\text{COOEt})_2$ , obtained by the action of chlorine on ethyl malonnate, is a colourless liquid (b. p.  $221^\circ$ ; sp. gr. = 1.185 at  $20^\circ$ ; water at  $15^\circ = 1$ ). On saponification with potash it gives only *potassium tartronate*,  $\text{CH}(\text{OH})(\text{COOK})_2$ .

*Tartronic acid*,  $\text{CH}(\text{OH})(\text{COOH})_2$ , obtained by decomposing the calcium salt with oxalic acid; melts at  $182^\circ$  with evolution of carbonic anhydride, leaving a *glycolide*, the aqueous solution of which on boiling with calcium carbonate, gave calcium glycolate.

The ethyl mono-substituted malonnates, on treatment with chlorine, give monochlorinated compounds.

*Ethyl monochlorisobutylmalonnate*,  $\text{C}_4\text{H}_9\text{CCl}(\text{COOEt})_2$ , (b. p.  $245^\circ$ , sp. gr. = 1.094 at  $15^\circ$ ). On saponification with potash, it gives *potassium isobutylhydroxymalonnate*,  $\text{C}_4\text{H}_9\text{C}(\text{OH})(\text{COOK})_2$ , the free acid of which decomposes on heating at  $150^\circ$  into carbonic anhydride and *hydroxyisobutylacetic acid*,  $\text{C}_4\text{H}_9\text{CH}(\text{OH}).\text{COOH}$ .

*Ethyl acetyltetracarbonate*,  $(\text{COOEt})_2\text{CH}.\text{CH}(\text{COOEt})_2$ , is obtained by the double decomposition of ethyl chloromalonnate and ethyl sodium malonnate. It crystallises in long brilliant white needles (m. p.  $75^\circ$ ; b. p.  $305^\circ$ , with slight decomposition). T. C.

**Inversion of the Optical Rotation of Ordinary Malic Acid.** By G. H. SCHNIDER (*Ber.*, 13, 620—623).—Ordinary malic acid has generally been considered as *laevorotatory*; if, however, the degree of concentration of a dilute aqueous solution of the acid, which is *laevorotatory*, be gradually increased, the specific rotation gradually diminishes until the percentage of acid is 34.24, when the optical activity entirely disappears; on further concentration the rotation becomes positive. The following interpolation formula,  $[\alpha]_D = 5.891 - 0.08959q$  ( $q$  = per cent. of water) shows that for pure anhydrous malic acid  $[\alpha]_D = +5.89$ .

Sodium malate behaves exactly like malic acid, the interpolation formula in this case being  $[\alpha]_D = 15.202 - 0.3322q + 0.0008184q^2$ , from which it follows that for the anhydrous salt  $[\alpha]_D = +15.2$ , and that a solution containing 47.43 per cent. of the salt is inactive. A



similar observation has been made in the case of tartaric acid (compare Boit, *Mémoires de l'Acad.*, 15, 208—211; *Ann. Chim. Phys.* [3], 29, 351, 366; Arndtsen, *ibid.* [3], 54, 415). T. C.

**Behaviour of Monochlorotetracrylic Acid on Fusion.** By A. GEUTHER (*Ber.*, 13, 242).—Kahlbaum (*Ber.*, 12, 2337) is mistaken in attributing to the author the statement that this acid is decomposed on fusion. It is partly decomposed by distillation. Ch. B.

**Nitrosothioglycollic Acid.** By R. MALY and R. ANDREASCH (*Ber.*, 13, 601—607).—*Nitrosothioglycollic acid*,  $\text{COOH}.\text{CH}(\text{NO}).\text{SH}$ , is obtained, together with cyanamide and dicyandiamide, by boiling 10 grams nitrosothiohydantoin (*ibid.*, 12, 967) with 60 grams of crystallised barium hydrate and 400 c.c. water, the reaction being in all respects analogous to that which occurs in the case of thiohydantoin (this Journal, 36, 712). The free acid was obtained as a crystalline mass, which is very easily soluble in ether, and is decomposed by

alcohol or water. The barium salt,  $\begin{array}{c} \text{CH}(\text{NO})\text{S} \\ | \\ \text{COO} \end{array} \text{Ba} + \text{H}_2\text{O}$ , is a crys-

talline powder or nodular mass which is insoluble in alcohol, sparingly soluble in cold water, but more easily in hot; it dissolves at once in dilute hydrochloric acid. It is gradually decomposed on heating above  $100^\circ$ . The other salts are mostly obtained by precipitation of the hot aqueous solution of the barium salt. The lead salt is a yellowish-white precipitate, which is insoluble in acetic acid and boiling water, and is not blackened by alkalis, but dissolves in hot soda to a clear liquid. The silver salt is a yellow precipitate, which rapidly blackens on exposure to light, and when freshly prepared is insoluble in ammonia and nitric acid. A dark violet colour is obtained when ferric chloride is added to a dilute solution of the barium salt, and this on addition of a drop of hydrochloric acid changes to a pure blue. On long standing, or on boiling, the colour disappears, because in both cases the nitrosothioglycollic acid is destroyed. Strong hydrochloric or nitric acid or stannous chloride produces this effect at once. This reaction is exceedingly sensitive and serves as a very ready method for detecting the acid. The free acid gives the blue colour at once on addition of ferric chloride. Nitrosothioglycollic acid, and acidified solutions of its salts are easily decomposed on heating into water and carbonic and sulphocyanic acids or their salts. The free acid is thus decomposed even at the ordinary temperature. T. C.

**Action of Zinc on Succinimide.** By C. A. BELL (*Ber.*, 13, 877—878).—Pyrrol is formed by the distillation of a mixture of succinimide and zinc-dust, and also by passing a current of hydrogen and succinimide vapour over platinum black at a temperature above the boiling point of the imide. When the vapour of ethyl succinimide is passed over zinc-dust at  $350^\circ$ , ethylpyrrol,  $\text{C}_4\text{H}_7\text{NEt}$ , is produced.

W. C. W.

**Contribution to a Knowledge of the Ureides.** By J. M. A. KRAMPS (*Ber.*, 13, 788—791).—E. Mulder having succeeded in obtain-

ing dibromothiohydantoin (*Ber.*, 8, 1263), the author was induced to repeat the researches of Claus and Neuhöffer (*Ber.*, 10, 825) on the action of chlorine and bromine on thiohydantoin. A stream of chlorine was slowly passed into a solution of thiohydantoin in hydrochloric acid, surrounded by a freezing mixture.

At the end of half an hour white flocculent crystals appeared, but on continuing the stream of gas they disappeared again. By stopping the gas at the proper moment, however, the crystals could be collected. They were found to consist of imperfectly shaped needles, insoluble in water, alcohol, and ether. They dissolve in alkalis with decomposition, and the solutions have a green fluorescence. They are also decomposed on heating to 110–120°. Their composition is represented by the formula,  $\text{CS} \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{OH} \\ | \\ \text{NH} \cdot \text{CO} \end{array} + \text{H}_2\text{O}.$

When excess of bromine was added to a solution of thiohydantoin under the same conditions as above, colourless crystals of dibromothiohydantoin were obtained. They are soluble in alcohol and ether, and are decomposed by hot water. Oxalic acid was found in the mother-liquor.

The author's method of obtaining thiohydantoinic acid differs somewhat from Maly's (*Ber.*, 10, 1849), inasmuch as he allows the aqueous solution of monochloroacetic acid and thiocarbamide to stand in the cold without neutralising the hydrochloric acid.

*Action of Monochloroacetyl-carbamide on Thiocarbamide.*—When these two bodies were dissolved in alcohol in equivalent quantities at 60–70°, large quantities of a nearly white flocculent body were obtained of the composition  $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 + \text{HCl}$ . This body is insoluble in alcohol and ether, and yields silky needles of thiohydantoin on addition of ammonia to its aqueous solution.

Monochloroacetyldimethylcarbamide and thiocarbamide when dissolved in alcohol at 70–80°, yield crystals of thiohydantoin hydrochloride, but in the cold, nodules made up of needles are formed, which consist of  $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CO} \cdot \text{NHMe} + \text{HCl}$ .

These crystals are decomposed by water into thiohydantoin hydrochloride and dimethylcarbamide.

G. T. A.

**Orthocymene.** By A. CLAUS and H. HANSEN (*Ber.*, 13, 897–899).—Orthocymene is formed by the action of sodium on a solution of orthobromotoluene and propyl bromide in absolute ether. The mixture is gently warmed, but when the reaction has commenced, it is cooled down to 10° in order to avoid the formation of ditolyl. At a temperature below 8°, considerable quantities of dipropyl are formed. Orthocymene is a colourless liquid (b. p. 181°). On treatment with sulphuric acid it yields two sulphonic acids; the formation of the  $\alpha$ -acid is favoured by a low, and that of the  $\beta$ - by a higher temperature. Both acids are very soluble in water, and are uncrystallisable. The  $\alpha$ -acid forms a sparingly soluble barium salt, which crystallises in glistening plates containing 1 mol.  $\text{H}_2\text{O}$ . The copper salt crystallises in dark-green needles containing  $4\text{H}_2\text{O}$ .

The potassium salt forms shining rhombic crystals.

The  $\beta$ -acid does not form crystalline salts. The  $\beta$ -sulphonic chloride is a syrupy liquid converted by ammonia into  $\beta$ -orthocymenesulphamide, which is deposited from an ethereal solution in glistening plates, and from an aqueous solution in brittle needle-shaped crystals.

W. C. W.

**Metacymene.** By A. CLAUS and T. STÜSSER (*Ber.*, 13, 899—901).—Metacymene prepared by the action of sodium at  $0^\circ$  on an ethereal solution of propyl bromide and metabromotoluene, is a colourless liquid which boils at  $176^\circ$  (sp. gr. 0.863 at  $16^\circ$ ).

Two sulphonic acids are formed by treating metacymene with sulphuric acid.

The  $\alpha$ -acid forms a sparingly soluble barium salt which crystallises in small plates, containing 1 mol.  $H_2O$ . The copper salt forms green hexagonal plates containing 4 mols.  $H_2O$ . The lead salt contains 3 mols.  $H_2O$ , and the calcium salt which crystallises in prisms 2 mols.  $H_2O$ . The potassium salt forms anhydrous needle-shaped crystals, which dissolve freely in water.

Barium  $\beta$ -cymenesulphonate crystallises in needles containing 1 mol.  $H_2O$ , which are freely soluble in hot water.

$\alpha$ -Metacymenesulphonic chloride prepared by heating the acid with phosphorus pentachloride in sealed tubes at  $140^\circ$ , is deposited from an ethereal solution in needle-shaped crystals (m. p.  $175^\circ$ ). The corresponding sulphamide does not crystallise.

W. C. W.

**Paracymene and Sulphuric Acid.** By A. CLAUS and C. CRATZ (*Ber.*, 13, 901—902).—When paracymene is treated with sulphuric acid at the ordinary temperature, two sulphonic acids are produced, viz., the well-known  $\alpha$ -paracymenesulphonic acid and a small quantity of a second acid, which is distinguished from the  $\alpha$ -acid by the greater solubility of its barium salt.

W. C. W.

**Oxidation of Dibromocymene.** By A. CLAUS and C. WIMMEL (*Ber.*, 13, 902—904).—On oxidation with a solution of chromic acid in glacial acetic acid, dibromocymene yields a new acid,  $C_{10}H_{10}Br_2O_4$ , which crystallises in glistening needles (m. p.  $152^\circ$ ) soluble in alcohol and ether. It forms crystalline salts, which dissolve freely in water. The barium salt contains 3 mols.  $H_2O$ . If a mixture of strong nitric acid (1 part) and water ( $1\frac{1}{2}$  parts) is used instead of chromic acid in the preparation of this substance, dibromoterephthalic acid and another acid are also formed.

If the oxidation is continued until the dibromocymene is completely destroyed, pure dibromoterephthalic acid,  $C_8H_4Br_2O_4$ , is obtained in white plates (m. p.  $320^\circ$ ) soluble in alcohol, ether, and glacial acetic acid.

The salts of this acid are very soluble in water and do not crystallise readily.

W. C. W.

**Compounds of Organic Bases with the Haloid Salts of Mercury.** By O. KLEIN (*Ber.*, 13, 834—835).—In addition to the bodies previously described (*Ber.*, 11, 743 and 1741; this Journal, Abst., 1878, 667; 1879, 231), the author has obtained compounds of aniline

and toluidine with mercuric bromide and iodide.  $\text{HgBr}_2 + 2\text{NH}_2\text{Ph}$  crystallises in white needles (m. p.  $110^\circ$ ) which are decomposed by boiling water.  $\text{HgI}_2 + 2\text{NH}_2\text{Ph}$  (m. p.  $60^\circ$ ) resembles the preceding compound, but is decomposed by treatment with alcohol. Mercuric bromide combines with 2 mols. paratoluidine, forming a substance crystallising in plates (m. p.  $120^\circ$ ) which are soluble in alcohol and ether, but are decomposed by hot water. The corresponding orthotoluidine compound also crystallises in plates, which begin to decompose at  $60^\circ$ , but melt at  $103^\circ$  if rapidly heated. The compounds of mercuric iodide with para- and ortho-toluidine resemble the compound with aniline. The former melts at  $81^\circ$ , the latter does not melt, but gives off orthotoluidine at  $40^\circ$ . W. C. W.

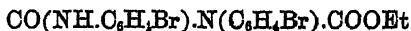
**Derivatives of Parabromaniline.** By M. DENNSTEDT (*Ber.*, 13, 228—238).—The following compounds have been prepared and examined:—

*Bromophenylurethane*,  $\text{C}_6\text{H}_9\text{NO}_2\text{Br}$  (m. p.  $84$ — $85^\circ$ ), is obtained by the action of ethyl chlorocarbonate on bromaniline dissolved in anhydrous ether. From dilute alcohol, it crystallises in white felted needles, insoluble in water, easily soluble in alcohol and ether.

*Bromophenylcyanate*,  $\text{C}_7\text{H}_4\text{NOBr}$ , is obtained by distilling the foregoing with phosphoric anhydride; m. p.  $39^\circ$ ; b. p.  $226^\circ$ . It is easily soluble in ether.

*Bromophenylmethyleurethane*,  $\text{C}_8\text{H}_9\text{O}_2\text{NBr}$ , is prepared by evaporating the methyl alcohol solution of the cyanate and crystallising from alcohol. It forms white needles, readily soluble in alcohol and ether; m. p.  $124^\circ$ .

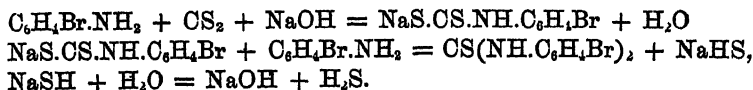
*Bromophenyl dicyanate*,  $\text{C}_{14}\text{H}_8\text{N}_4\text{O}_2\text{Br}_2$ , a dimolecular compound of the cyanate, analogous to Hofmann's phenyl dicyanate (*Annalen*, Supp., 1, 57; and *Ber.*, 4, 246), is obtained when the cyanate, melted on a water-bath, is stirred with a glass rod moistened with triethylphosphine. After long boiling with absolute alcohol it dissolves, and on cooling, white needles of *ethyl dibromophenyl allophanate*,



(m. p.  $153^\circ$ ), separate. The latter may be crystallised from anhydrous ether.

*Dibromophenylbiuret*,  $\text{NH}(\text{CO}.\text{NH}.\text{C}_6\text{H}_4\text{Br})_2$ , is formed when the pulverised dicyanate is allowed to stand with alcoholic ammonia. It begins to sublime (without melting) at  $240^\circ$ , and decomposes at  $280^\circ$ . It is insoluble in water, sparingly soluble in alcohol and ether.

*Bromophenylthiocarbimide*,  $\text{CSN}.\text{C}_6\text{H}_4\text{Br}$ , has been prepared by Otto (*Ber.*, 2, 408) by distilling dibromophenylthiocarbamide with phosphoric anhydride. The amide is formed with extreme slowness when bromaniline is boiled with an alcoholic solution of carbon bisulphide in theoretical quantity. The process is much hastened by adding a little moderately strong caustic soda solution (a few c.c. for 40 grams bromaniline). The amide separates partly after an hour's boiling, and the reaction is completed in six or seven hours. The caustic soda perhaps assists by inducing the following reactions:—



*Monobromophenylthiocarbamide*,  $\text{C}_7\text{H}_7\text{N}_2\text{SBr}$ , is formed by treating the thiocarbimide with alcoholic ammonia. It forms needles (m. p.  $183^\circ$ ) insoluble in water, soluble in alcohol and ether.

*Phenylbromophenylthiocarbamide*,  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{SBr}$ , obtained by boiling the thiocarbimide with alcoholic solution of aniline, forms colourless needles (m. p.  $158^\circ$ ), which are tolerably soluble in cold, very soluble in hot alcohol or ether.

*Hemithiobromophenylurethane*,  $\text{C}_9\text{H}_{10}\text{NOSBr}$ , is formed by heating the thiocarbimide with absolute alcohol at  $120^\circ$  for several hours. Slender slightly yellow needles, insoluble in water, easily soluble in alcohol and ether. M. p.  $105^\circ$ .

*Thiobromophenylurethane*,  $\text{C}_9\text{H}_{10}\text{S}_2\text{NBr}$ , is prepared by heating the thiocarbimide with ethyl mercaptan at  $140^\circ$ . It is insoluble in water, soluble in alcohol or ether. M. p.  $89^\circ$ .

*Isocyanomonobromophenyl chloride*,  $\text{C}_7\text{H}_4\text{NBrCl}_2$ , analogous to Sell and Zierold's isocyanophenyl chloride (*Ber.*, 7, 1228), is obtained by acting with chlorine on bromophenylthiocarbimide. It is a yellowish heavy liquid (b. p.  $255-256^\circ$ ). By the action of bromaniline, it yields the hydrochloride of a base,  $\text{C}_6\text{H}_4\text{Br.N}:\text{C}(\text{NH.C}_6\text{H}_4\text{Br})_2.\text{HCl}$ , isomeric with tribromophenylguanidine. This salt is crystallisable from dilute alcohol, is very soluble in alcohol and ether, and when treated with ammonia yields the free base as an uncrystallisable gummy mass. The platinochloride forms bright yellow plates.

*Ethenyldibromophenyldiamine*,  $(\text{C}_2\text{H}_3)(\text{C}_6\text{H}_4\text{Br})_2\text{HN}_2$ , is prepared by acting with phosphorus chloride on a mixture of bromaniline and acetic acid, heating for some time at  $160^\circ$ , extracting with water, and precipitating with ammonia. It is a white thick liquid. Only the hydrochloride and platinochloride were analysed.

*Formobromanilide*,  $\text{CHO.NH.C}_6\text{H}_4\text{Br}$  (m. p.  $119^\circ$ ) is obtained by heating ethyl formate with bromaniline at  $100^\circ$ . It is insoluble in cold water, with difficulty soluble in hot water, readily soluble in alcohol or ether. It may also be prepared by the action of bromine water on formanilide rubbed up with water. Measurements of the crystals, which belong to the rhombic system, are given.

*Thioformobromanilide*,  $\text{CHS.NH.C}_6\text{H}_4\text{Br}$ , is prepared from the above in the same way as thioformanilide from formanilide (Hofmann, *Ber.*, 11, 338). It is soluble in hot alcohol and ether, and melts with decomposition at  $189-190^\circ$ .

*Bromophenyglycocine*,  $\text{CH}_2(\text{NH.C}_6\text{H}_4\text{Br}).\text{COOH}$ , is obtained by warming an ethereal solution of 2 mols. bromaniline and 1 mol. chloracetic acid. It is very unstable, and exceedingly soluble in alcohol, ether, and hot water. With suitable precautions it may be crystallised from the latter; m. p.  $98^\circ$ . It forms a bright green copper salt.

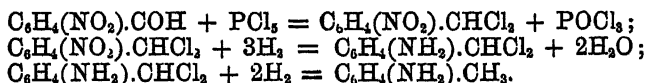
*Dibromophenylazethylenecarbamide*, the bromanilide of bromophenyglycocine,  $\text{C}_6\text{H}_4\text{Br.NH.CH}_2.\text{CO.NH.C}_6\text{H}_4\text{Br}$ , is prepared by boiling bromaniline monochloracetate with excess of bromaniline (*vide*

Meyer, *Ber.*, 8, 1152), or by adding 1 mol. chloracetic chloride to an ethereal solution of 4 mols. bromaniline. It is soluble in alcohol and ether, insoluble in cold, sparingly soluble in hot water. It sublimes at 145°, and melts between 154° and 161°.

*Ethyl bromophenylamidoacetate*,  $C_6H_4Br.NH.CH_2.COOEt$  (m. p. 95–96°), is prepared by gently heating 1 mol. of ethyl monochloracetate with 2 mols. bromaniline. It is sparingly soluble in cold, easily soluble in hot alcohol or ether, and is insoluble in water.

Ch. B.

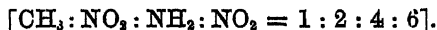
**Metatoluidine.** By O. WIDMAN (*Ber.*, 13, 676–678).—This compound (b. p. 197–200°) may be obtained in large quantity by the action of phosphorus pentachloride on metanitrobenzaldehyde, the resulting metanitrobenzal chloride being reduced with zinc and hydrochloric acid thus:—



*Metanitrobenzal chloride*,  $C_6H_4(NO_2).CHCl_2$ , crystallises from alcohol either in colourless thin four- or six-sided plates or in white needles (m. p. 65°), which are easily soluble in boiling alcohol and in ether, but insoluble in water.

T. C.

**Dinitroparatoluidine.** By F. BEILSTEIN (*Ber.*, 13, 242–244).—Tiemann (*Ber.*, 3, 218) states, and it is commonly believed that the dinitroparatoluidine (m. p. 168°), which he obtained by reducing trinitrotoluene, is identical with the base (m. p. 166°) which the author and Kuhlberg (*Annalen*, 158, 341) obtained by nitrating paracetoluidine and saponifying. This is erroneous. On nitrating paratoluidine, the first product is metanitroparatoluidine [ $CH_3:NO_2:NH_2 = 1:3:4$ ]. Since a second nitro-group entering the molecule should take the para-position with respect to the first, dinitroparatoluidine must have the constitution [ $CH_3:NO_2:NH_2:NO_2 = 1:3:4:5$ ], and the nitrogenous groups must be neighbouring; but on nitrating [1:2:4] dinitrotoluene, a trinitrotoluene [1:2:4:6] should be obtained for the same reason. And if, as in the case of dinitrotoluene, reducing agents first attack the paranitro-group, the dinitrotoluidine prepared from it must have the constitution



The nitrogen groups must be symmetrical.

Independently of those theoretical considerations, there is also experimental evidence of the difference of the two compounds, although their physical properties appear to be the same. The author finds that they behave differently towards oxidising agents. Friederici has shown (*Ber.*, 11, 1976), and the author confirms his statements, that Tiemann's dinitroparatoluidine is slowly converted by boiling chromic mixture into dinitroparamidobenzoic (chrysammic) acid. But symmetrical dinitroparatoluidine is much more energetically attacked by chromic mixture, and does not yield a trace of chrysammic acid. The

product is an indifferent amorphous insoluble powder, probably an azo-compound.

Symmetrical dinitrotoluidine is best prepared by gradually adding the theoretically necessary quantity of a concentrated aqueous solution of ammonium hydrosulphide to 1 part of trinitrotoluene well rubbed up with 2 parts of alcohol, allowing to stand, precipitating with water, and extracting repeatedly with boiling hydrochloric acid (sp. gr. 1.05). The base is then precipitated by ammonia, dissolved in chloroform, and crystallised from 50 per cent. acetic acid, or from hydrochloric acid sp. gr. 1.055 (m. p. 166.5—168°). It is soluble in alcohol, acetic acid, benzene, and chloroform, sparingly soluble in boiling water, insoluble in light petroleum. Ch. B.

**Condensation Products of Tertiary Aromatic Bases.** By O. FISCHER (*Ber.*, 13, 807—809).—Dimethyl*para*toluidine has no action on benzaldehyde in presence of zinc chloride even at 120—130°. Dimethyl*ortho*toluidine yields a small quantity of a base, the constitution of which has not been ascertained. Dimethyl*meta*toluidine acts with great energy, even at the temperature of the water-bath, and yields a base which is analogous to tetramethyldiamidotriphenylmethane. Neither of these bases affords a colouring matter on oxidation. According to the author's experience, no *para* substitution product of dimethylaniline yields condensation products with aldehydes, alcohols, &c., and the same seems to be the case with dimethyl*para*toluidine.

Benzaldehyde and dimethyl*meta*toluidine in presence of zinc chloride yield a base  $C_{22}H_{20}N_2$ , which crystallises in large prisms (m. p. 109°). It is soluble in mineral acids, but is reprecipitated by sodium acetate. It is easily soluble in benzene, alcohol, and ether, but is insoluble in water. The platinochloride of this base consists of fine golden-yellow crystals. No colouring matter was obtained on oxidation of the base.

A new reaction of dimethylaniline is also described in the paper. When benzoic anhydride is gently warmed with dimethylaniline in presence of zinc chloride, a fine green colouring matter is obtained, having the appearance of malachite. G. T. A.

**A New Class of Ammonium Compounds. Part I.** By P. GRIESS (*Ber.*, 13, 246—250).—By acting with methyl iodide in excess on the isomeric amidophenols, the author has obtained new bases, to

which he assigns the constitution  $C_6H_5 \begin{array}{c} \diagup O \\ | \\ NMe_3 \end{array}$ .

*Orthotrimethylphenolammonium*,  $C_6H_3 \begin{array}{c} \diagup O \\ | \\ NMe_3 \end{array} + H_2O$ , is prepared by

mixing a cold methyl alcohol solution of orthamidophenol hydrochloride with three parts of methyl iodide, and adding concentrated potash solution to strongly alkaline reaction. Potassic chloride separates out, and on allowing the mixture to stand its reaction becomes acid. More potash is then added, and this addition is repeated as long as an acid reaction appears on standing. When the action is completed,

the alcohol is distilled off, the solution acidified with hydriodic acid, and the yellowish crystals of the hydriodide which separate are crystallised from boiling water with addition of animal charcoal. The crystals are then dissolved in water, decomposed by silver oxide or carbonate, and the solution evaporated on the water-bath, when a syrup remains which solidifies on standing. The pressed and recrystallised base forms white prisms, which are soluble in water and alcohol, but insoluble in ether: by the latter the base may be separated from its alcoholic solution. Its taste is intensely bitter. It is not acted on by potash or ammonia, but combines with acids (excepting carbonic acid) to form two classes of salts. The iodide,



the constitution of which is possibly  $C_6H_4(OH).NMe_3I + H_2O$ , crystallises in white indistinct prisms, very soluble in hot water. When ammonia is added to an aqueous solution of this salt, a sparingly soluble hemi-iodide,  $(C_6H_5NO)_2.HI$ , separates in needles. From alcohol, it separates in thick prisms. The base also forms a very soluble crystalline hydrochloride,  $C_6H_5NO.HCl + 2H_2O$ ; a reddish-grey nitroprusside,  $(C_6H_5NO)_2.H_2FeCy_5(NO)$ ; a yellowish-red platinochloride,  $(C_6H_5NO.HCl)_2.PtCl_4$ ; and a brown periodide, with green reflection, which is insoluble in water.

Heat acts on the base as on the aromatic betaines. When distilled, it passes into the isomeric *orthodimethylamido-anisol*,  $C_6H_4(OMe).NMe_2$ , a colourless strongly refracting basic oil, of peculiar odour and burning biting taste. This forms a deliquescent crystalline hydrochloride, and a sparingly soluble platinochloride. It resembles dimethylaniline, and like that body is capable of conversion into colouring matters, which the author is engaged in investigating.

When orthotrimethylphenolammonium hydrochloride is distilled, it breaks up into methyl chloride and orthodimethylamidophenol,  $C_6H_4(OH).NMe_2$  (m. p.  $45^\circ$ ). The latter is crystalline, very sparingly soluble in boiling water, easily in alcohol, ether, acetic acid, and potash solution. Its taste, at first biting, is afterwards bitter. Ferric chloride colours its solutions red-violet. The hydrochloride dries up to a gum: from its solution, ammonia precipitates the base as an oil, which solidifies to small white rhombic crystals.

*Paratrimethylphenolammonium*,  $C_6H_5 \begin{array}{c} \diagup O \\ | \\ \diagdown NMe_3 \end{array} + H_2O$ , crystallises in

clear six- or eight-sided tables. It strongly resembles its isomeride, and on distillation yields paradimethyl-amidoanisole,  $C_6H_4(OMe).NMe_2$  (m. p.  $48^\circ$ ), which crystallises from alcohol in white rhombic leaflets.

Attempts to obtain similar bases by means of ethyl iodide were unsuccessful. Ch. B.

**A New Class of Ammonium Compounds. Part II.** By P. GRIESS (*Ber.*, 13, 647—650).—*Trimethylnitrophenolammonium*,

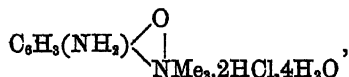
$C_6H_3(NO_2) \begin{array}{c} \diagup O \\ | \\ \diagdown NMe_3 \end{array}$ , is obtained by the action of methyl iodide on



Laurent and Gerhardt's amidonitrophenol, the process being conducted as previously described in the case of the other triphenylammonium bases, except that the free base is best obtained from its salts by the use of potash in place of oxide of silver. Trimethylnitrophenolammonium crystallises from water in brilliant yellow needles or tables, having a strongly bitter taste. It is only sparingly soluble in cold water or alcohol, but more easily in these liquids when hot. It is insoluble in ether and in benzene. It has no action on vegetable colours. Heated above  $200^{\circ}$ , it is decomposed, without previous fusion, into a residue of carbon and a reddish volatile oil. It is a strong base.

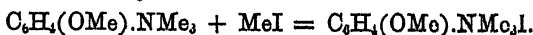
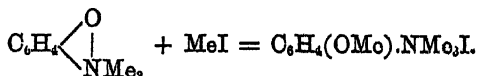
*Trimethylnitrophenolammonium iodide*,  $C_6H_5N_2O_3.HI.2H_2O$ , crystallises in white needles, which are moderately soluble in hot, but only sparingly soluble in cold water. The *hydrochloride*,  $C_6H_5N_2O_3.HCl.H_2O$ , crystallises in prisms, which behave towards solvents like the hydriodide. The *platinochloride*,  $(C_6H_5N_2O_3.HCl)_2.PtCl_4.6H_2O$ , forms bright yellow needles or rhombic plates, which are sparingly soluble in boiling water, hardly at all in cold water, and almost insoluble in alcohol. The *periodate* crystallises in small brown needles.

*Trimethylamidophenolammonium hydrochloride*,



is obtained by the reduction of the corresponding nitro-compound with tin and hydrochloric acid. It crystallises in white plates, which are easily soluble in water or alcohol, even when cold, also in ether. With ferric chloride, it gives a deep violet colour. The *platinochloride*,  $C_6H_5N_2O_3.2HCl.PtCl_4 + 2H_2O$ , forms small rhombic or six-sided prisms, which are only sparingly soluble in cold water, and are decomposed by boiling water.

*Orthotrimethylanisolammonium iodide*,  $C_6H_4(OMe).NMe_3I$ , is obtained by the action of methyl iodide on a solution of orthotrimethylphenolammonium in methyl alcohol, to which a little potash has been added, or by the action of methyl iodide on dimethylamido-anisol, thus:—



It crystallises in long white needles, which are easily soluble in hot, but only sparingly soluble in cold alcohol or water. The *platinochloride*,  $(C_{10}H_8NOCl)_2 + PtCl_4$ , forms brilliant yellow plates or six-sided tables, which are only very sparingly soluble in cold water. The *hydrate*,  $C_6H_4(OMe).NMe_3.OH$  (?), is obtained by the action of silver oxide on the iodide. It is strongly alkaline, and gradually decomposes on warming into orthodimethylamido-anisol and methyl alcohol.

*Paratrimethylanisolammonium iodide*,  $C_6H_4(OMe).NMe_3I$ , is obtained like the ortho-compound, using para- instead of ortho-trimethylphenolammonium. It crystallises in four- or six-sided plates. The *platinochloride*,  $C_{10}H_8(NOCl)_2 + PCl_4$ , consists of small yellow six-sided prisms. Both the above compounds behave towards solvents like the

corresponding ortho-compounds. The *hydrate* is similar to the ortho-compounds, and on heating splits up into paradimethylamidoanisol and methyl alcohol. T. C.

**Formation of Diamines.** By A. BERNTHSEN and F. SZYMANSKI (*Ber.*, 13, 917—919).—*Benzylidenemonophenyldiamine*,

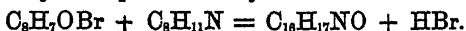


is formed, together with several other bases, when an alcoholic solution of benzenylmonophenylamidine is treated with sodium amalgam. The liquid is from time to time neutralised with strong acetic acid, and the reduction is stopped as soon as the formation of ammonium amalgam commences.

The bases are separated by recrystallising their hydrochlorides, when benzyldienemonophenyldiamine hydrochloride,  $\text{C}_{13}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$ , is deposited in thick prisms (m. p.  $234^\circ$ ) soluble in alcohol and water. The platinochloride crystallises in long needles, and also in rhombic plates.

The free base is insoluble in water, but dissolves freely in other solvents. It melts at  $115^\circ$ , and distils without decomposition. On reduction, it yields benzylaniline. W. C. W.

**New Synthesis of Organic Bases containing Oxygen.** By W. STAEDEL and O. SIEPERMANN (*Ber.*, 13, 841—844).—When bromoacetylbenzene,  $\text{Ph} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$  (1 mol.), is dissolved in dimethylaniline (2 mols.), a reaction takes place, and the liquid solidifies on cooling, forming a crystalline product, soluble in hot alcohol. The alcoholic solution deposits yellow prismatic crystals of the new base,  $\text{C}_{16}\text{H}_{17}\text{NO}$ .



Colourless crystals of the hydrobromide of another base can be obtained from the mother-liquor. The base,  $\text{C}_{16}\text{H}_{17}\text{NO}$ , is insoluble in water, but dissolves sparingly in alcohol and ether, and freely in benzene and toluene. It melts with partial decomposition at  $120^\circ$ .

The base is also soluble in dilute hydrochloric and sulphuric acids, but is reprecipitated when these solutions are diluted with water. The hydrochloric acid solution forms precipitates with picric, phosphomolybdic, and tannic acids, also with potassium, mercuric iodide, and with platinum and stannous chlorides.

The platinochloride,  $(\text{C}_{16}\text{H}_{17}\text{NOHCl})_2\text{PtCl}_4$ , crystallises in plates. Ferric chloride or dilute nitric acid readily oxidises the base. By the action of methyl iodide the compound  $\text{C}_{16}\text{H}_{17}\text{NO} \cdot \text{MeI}$  is obtained. It is purified by digestion with ether, and recrystallisation of the insoluble portion from water. By treatment with silver oxide, the iodine is removed from this substance, and a strongly alkaline liquid is produced, which forms crystalline salts.

Bromoacetylbenzene also acts in a similar manner on dimethylmetatoluidine and on tetramethylmetaphenylenediamine.

The compound from dimethylaniline probably has the constitution  $\text{Ph} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , and the dimethylmetatoluidine derivative may be represented as  $\text{C}_6\text{H}_3(\text{Ph} \cdot \text{CO} \cdot \text{CH}_2\text{Me})(\text{NMe})_2 = [5 : 1 : 3]$ .

W. C. W.

**Synthesis of Leucaniline.** By O. FISCHER and P. GREIFF (*Ber.*, 13, 669—671).—Paranitrobenzaldehyde (m. p. 98°) is converted into a yellow crystalline nitro-base when digested with aniline hydrochloride and zinc chloride at 120°. This compound dissolves in acids, forming colourless solutions, and on reduction with zinc-dust and acetic acid gives paraleucaniline. The paranitrobenzaldehyde employed in the above reaction was prepared by the action of lead nitrate and nitric acid on paranitrobenzyl chloride.

The following are good lecture experiments:—Rosaniline is obtained when a hot alcoholic solution of chloranil is poured into a hot freshly prepared solution of leucaniline in alcohol. Tetramethyldiamidotriphenylmethane gives benzaldehyde green under similar circumstances. Other leuco-bases also behave in a similar manner.

T. C.

**Some Compounds of the Leuco-base from Cuminol and Dimethylaniline.** By J. ZIEGLER (*Ber.*, 13, 786—788).—The best method of obtaining the base described by O. Fischer (*Ber.*, 12, 1688) is to digest cuminal and dimethylaniline for a day with zinc chloride and a little water at 120°. The *hydrochloride* is obtained by passing a stream of dry hydrochloric acid gas into a solution of the base in anhydrous ether or light petroleum. A white crystalline and extremely hygroscopic powder separates out. When dried over sulphuric acid in a vacuum it consists of  $C_{26}H_{32}N_2 \cdot 2HCl$ .

The *picrate*,  $C_{26}H_{32}N_2 + 2C_6H_3(NO_2)_3 \cdot OH$  (m. p. 156°), is formed when an alcoholic solution of the base is mixed with picric acid. It consists of fine green crystals, which explode when heated to 220°.

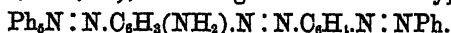
The *methiodide*,  $C_{26}H_{32}N_2 \cdot 2CH_3I$ , obtained by heating the base for a day at 115° with methyl iodide and methyl alcohol under pressure, consists of snow-white crystals (m. p. 200°), easily soluble in hot water.

The *platinochloride*,  $C_{26}H_{32}N_2(HCl)_2 + PtCl_4$ , is a yellow crystalline body, which is sparingly soluble in water, and still less so in alcohol and ether.

When the base is mixed with strong nitric acid and the solution diluted with water, a yellowish body is obtained, which on repeated crystallisation from acetic acid yields bright yellow acicular crystals (m. p. 206°). Apparently it is a hexnitrotetramethyldiamidotriphenylmethane. The leuco-base yields colouring matters on oxidation, which closely resemble the green from benzaldehyde. The picrate is most easily purified. All the salts of the colouring matter are characterised by a bright red metallic lustre.

G. T. A.

**Supplementary Notice on New Colouring Matters.** By W. v. MILLER (*Ber.*, 13, 803).—Compounds similar to those described by the author have been obtained by Caro and Schraube, and also by Griess (*Annalen*, 137, 84), who assigned to them the type—



G. T. A.

**Homologues of Phosphenyl Chloride.** By A. MICHAELIS and C. PANEK (*Ber.*, 13, 653—656).—*Phostolyl chloride*,  $C_7H_7PCl_2$ . The

presence of a small quantity of water is necessary in the formation of this compound from a mixture of phosphorus trichloride, toluene, and aluminium chloride (*ibid.*, 12, 1009); the best yield (56 grams) is obtained by taking the following proportions:—150 grams toluene, 200 grams phosphorus trichloride, 30 grams aluminium chloride, and 1 c.c. water. Pure phostolyl chloride forms crystalline masses of long needles (m. p.  $20^{\circ}$ , b. p.  $245^{\circ}$ ). *Tolylphosphorous acid*,  $C_7H_7PO_2H_2$ , is obtained by decomposing phostolyl chloride with water; it crystallises from alcohol in monoclinic tables (m. p.  $104^{\circ}$ ). *Tolylphosphinic acid*,  $C_7H_7PO_3H_2$ , crystallises in needles (m. p.  $188^{\circ}$ ). *Phostolyl tetrachloride*,  $C_7H_7PCl_4$ , is obtained by the direct combination of chlorine with phostolyl chloride. On heating in sealed tubes at  $200^{\circ}$  it gives monochlorobenzyl chloride, phosphorus trichloride, phostolyl chloride, and hydrochloric acid,  $2C_7H_7PCl_4 = C_7H_7Cl_2 + C_7H_7PCl_2 + PCl_3 + 2HCl$ . This does not decide whether phostolyl chloride is  $Ph.CH_2.PCl_2$ , or  $C_6H_4Me.PCl_2$ , although as the reaction only takes place at  $200^{\circ}$  it appears more probable that the chlorine attacks the methyl radicle, and that the compound is a true phostolyl chloride.

*Phosylochloride*,  $C_6H_5PCl_2$ , and the acids  $C_6H_5PO_2H_2$  and  $C_6H_5PO_3H_2$ , have also been prepared. T. C.

**Bromonitro- and Bromamido-anisöl.** By W. STAEDEL and G. DAMM (*Ber.*, 13, 838—839).—*Monobromoparanitranisöl*,



prepared by heating potassium monobromoparanitrophenate with methyl iodide and methyl alcohol, crystallises in white needles (m. p.  $106^{\circ}$ ), soluble in alcohol and ether. On reduction with tin and hydrochloric acid it yields *monobromoparanisidine hydrochloride*. The free base,  $C_6H_4Br(NH_2).OMe$ , is an oily liquid, insoluble in water, but dissolving freely in alcohol and ether. Its salts are crystalline.

*Dibromoparanisidine*,  $C_6H_4Br_2(NH_2).OMe$ , prepared by the reduction of dibromoparanitranisöl (m. p.  $126^{\circ}$ ) is a white solid body, soluble in alcohol, ether, and benzene. It combines with hydrochloric, sulphuric, and oxalic acids, forming salts, which crystallise in white needles. W. C. W.

**Orthanisidine.** By O. MÜLHAUSER (*Ber.*, 13, 919—924).—*Orthanisidine*,  $NH_2.C_6H_4.OMe$ , prepared by the reduction of orthonitranisöl (b. p.  $276.5^{\circ}$ ) by ammonium sulphide, boils at  $228^{\circ}$ . The hydrochloride, hydrobromide, and acid sulphate, form colourless crystals, soluble in water and alcohol. The neutral sulphate has not yet been obtained. *Acetaniside*,  $NHAc.C_6H_4.OMe$ , formed by the action of acetic anhydride on anisidine, is a pearly, crystalline substance, soluble in glacial acetic acid and in hot water. It melts at  $79^{\circ}$ , and boils at  $305^{\circ}$ . When water is added to a solution of this compound in strong nitric acid, *dinitracetaniside*,  $NHAc.C_6H_4(NO_2)_2.OMe$  is precipitated. On recrystallisation from alcohol, it is obtained in yellow crystals (m. p.  $147^{\circ}$ ). *Dianisylcarbamide* and anisidine hydrochloride are deposited when carbonyl chloride is passed through a solution of anisidine in benzene. After removing the latter substance by treat-

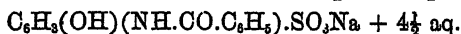
ment with dilute hydrochloric acid, the carbamide is recrystallised from alcohol. The crystals which are colourless melt at  $174^{\circ}$ . *Monanisylcarbamide*,  $\text{NH}_2\text{CO.NH.C}_6\text{H}_4\text{OMe}$ , prepared by the action of potassium cyanate on an aqueous solution of anisidine hydrochloride, forms colourless crystals (m. p.  $146.5^{\circ}$ ), soluble in hot water and alcohol.

*Dianisylthiocarbamide*,  $\text{SC(NH.C}_6\text{H}_4\text{OMe)}_2$ , produced by warming anisidine and alcoholic potash with an excess of carbon bisulphide, crystallises in white needles (m. p.  $134.5^{\circ}$ ) soluble in hot alcohol. *Monanisylthiocarbamide*,  $\text{NH}_2\text{CS.NH.C}_6\text{H}_4\text{OMe}$ , is precipitated on warming a mixture of anisidine hydrochloride and potassium thiocyanate. It crystallises in needles, which melt at  $152^{\circ}$ .

On oxidation with chromic mixture, anisidine yields a substance which forms yellow crystals (m. p.  $138^{\circ}$ ) having a penetrating odour.

W. C. W.

**Benzamidophenolsulphonic Acids and Amides of the Amidophenolsulphonic Acids.** By J. POST and L. HOLST (*Ber.*, 13, 617—619).—The same hydrogen atom is replaced by the  $\text{HSO}_3$  group, whether nitrophenol (ortho- or para-) or the corresponding amidophenol is converted into the sulphonic compound. This can be best shown in the case of the benzamidophenolsulphonic acids, as they form well characterised salts. These benzoic derivatives are obtained in the ordinary way by the use of benzoic chloride. For the preparation of the anilides of the amidophenolsulphonic acids, the unstable sulphochlorides are first obtained by the action of phosphorus pentachloride, and then converted into the more stable anilides by means of aniline. The compounds (both in the ortho- and para-series) derived from nitrophenol and from the corresponding amidophenol, are in all cases identical. *Sodium benzamidophenolsulphonate*,



crystallises in needles, which are easily soluble in water and alcohol. *Barium salt*  $[\text{C}_6\text{H}_3(\text{OH})(\text{NH.CO.C}_6\text{H}_5).\text{SO}_3]_2\text{Ba}$ , crystallises in brilliant, colourless spangles, which are sparingly soluble in alcohol and water. *Strontium salt* crystallises with  $4\frac{1}{2}$  aq. in colourless, scaly crystals, which are very sparingly soluble in water and alcohol. *Calcium salt* also crystallises with  $4\frac{1}{2}$  aq. and is similar to the strontium salt. *Anilide of amidophenolsulphonic acid*,



forms colourless needles (m. p.  $205^{\circ}$ ), which are easily soluble in alcohol, glacial acetic acid, and benzene, but insoluble in ether and in light petroleum. All the above compounds are derived from orthamidophenolsulphonic acid. The *anilide of paramidophenolsulphonic acid*,  $\text{C}_6\text{H}_3(\text{OH})\text{NH}_2.\text{SO}_2\text{NHPh}$ , derived from paramidophenolsulphonic acid, consists of colourless, compact crystals (m. p.  $98^{\circ}$ ), which are easily soluble in alcohol, glacial acetic acid, and benzene, but insoluble in light petroleum and in ether.

T. C.

**$\alpha$ -Dinitrophenyl Ether.** By C. WILLGERODT (*Ber.*, 13, 887).— *$\alpha$ -Dinitrophenyl ether*,  $\text{O(C}_6\text{H}_3\text{NO}_2)_2$  [1 : 2 : 4] is prepared by

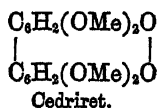
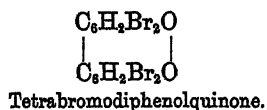
heating equal parts of potassium  $\alpha$ -dinitrophenate and  $\alpha$ -dinitrochlorobenzene, in sealed tubes at 150—200°. The crude product is washed with water, and boiled with alcohol to remove impurities. The pure residue is a colourless, crystalline substance (m. p. 195°), soluble in hot amyl alcohol, benzene, chloroform, and glacial acetic acid, but insoluble in alcohol. Boiling potash converts it into potassium dinitrophenate.

W. C. W.

**Oxidation of Substituted Phenols.** By C. MAGATTI (*Ber.*, 13, 224—228).—In his paper on the ethylenic ethers of pyrogallol (*Ber.*, 12, 1860) the author stated that by oxidising diphenol in solution in glacial acetic acid, he had obtained a brown amorphous substance, which dissolved with blue colour in concentrated sulphuric acid. This substance he suspected to be the simplest analogue of cedriret; but he has not been able to obtain it in a form suitable for analysis. It is not formed if the acetic acid solution is heated, nor if nitric acid is used as the oxidant. An alcoholic solution of diphenol also gives a violet precipitate, soluble with blue colour in sulphuric acid.

A better result is obtained by oxidising *tetrabromodiphenol*. To prepare this body, bromine is added to diphenol dissolved in warm acetic acid until the colour no longer disappears, and the mixture is heated. Tetrabromodiphenol,  $C_{12}H_6Br_4O_2$ , then separates in felted needles, which may be purified by repeated crystallisations from absolute alcohol (m. p. 264°). It is insoluble in water, sparingly soluble in alcohol, ether, and sulphuric acid, but is easily dissolved by alkalis. By digestion with acetic anhydride and sodium acetate for two hours, it is converted into a diacetyl derivative,  $C_{12}H_4Ac_2Br_4O_2$  (m. p. 245°).

Oxidising agents differ in their action on tetrabromodiphenol. Potassium dichromate and nitric acid give red precipitates in the acetic acid solution; potassium ferricyanide gives a blue, and bromine water a dirty brown precipitate with its solution in alkali. All these precipitates are soluble in strong sulphuric acid with blue colour, soon passing into brown; but none could be obtained pure. When, however, a little red fuming nitric acid is added to a solution of 3 grams of tetrabromodiphenol in 100 of acetic acid, and heated to 95°, the mixture becomes deep red, and on cooling deposits crystalline scales, which are dark red-brown by transmitted light, deep steel-blue by reflected light. This substance has the composition  $C_{12}H_4Br_4O_2$ . It is insoluble in all the ordinary menstrua, and cannot be fused without decomposition. Its solution in sulphuric acid is violet, and gives a brick-red precipitate on the addition of water. Digestion with sulphurous acid reconverts it into tetrabromodiphenol. It has doubtless a constitution analogous to that of cedriret, and may be named *tetrabromodiphenolquinone*.



The compound obtained from triiodophenol by Kämmerer and Benziger (*Ber.*, 11, 557) is possibly similarly constituted.

*Tetrachlorodiphenol*,  $C_{12}H_4Cl_4O_2$  (m. p.  $233^\circ$ ), is easily prepared by treating diphenol, suspended in much acetic acid, with a stream of chlorine. The diphenol is soon dissolved, and the chlorine compound subsequently separates. After washing with acetic acid and crystallisation from highly dilute alcohol, it forms transparent needles. Treated as above described with a little nitric acid, it yields tetrachlorodiphenolquinone,  $C_{12}H_2Cl_4O_2$ , having all the characters of the bromine compound, but giving a blood-red solution with sulphuric acid. This solution becomes colourless when slowly heated to  $100^\circ$ , and deposits a body which crystallises in needles. Ch. B.

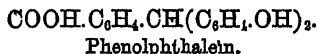
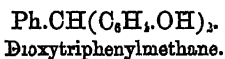
**Compounds of Benzotrichloride with Phenols and Tertiary Aromatic Bases.** By O. DOEBNER (*Ber.*, 13, 610—614).—The name benzein is proposed for the class of compounds described in former communications (*ibid.*, 11, 1236; 12, 1462).—*Resorcinolbenzein* is obtained by gently warming 1 mol. benzotrichloride with 2 mols. resorcinol, finally on a paraffin-bath at  $180$ — $190^\circ$ . The product is extracted with water, to take up unchanged resorcinol, the residue dissolved in soda, and then precipitated by acetic acid. The yellow crystalline product thus obtained is recrystallised from a mixture of alcohol and glacial acetic acid, from which resorcinolbenzein separates in large prisms. These crystals appear yellow by transmitted, and violet-red by reflected light; an analysis of the substance dried at  $100^\circ$  led to the formula  $C_{18}H_{10}O_7$ . The compound, when precipitated from alkaline solution by an acid, is easily soluble in alcohol, whilst the crystals obtained as above described are only very sparingly soluble in this solvent, but more easily on the addition of an acid. This solution has a yellowish-red colour, and fluoresces like fluorescein. By quick cooling of the acid alcoholic solution, the compound separates as concentric groups of yellow needles, but by slow cooling the prisms above described are obtained. It is insoluble in water, ether, and benzene. On heating at  $130^\circ$  it loses water, and then has the composition  $C_{18}H_{10}O_7 = 2(C_{12}H_4O_4 + H_2O)$ ; at temperatures above  $200^\circ$  further decomposition occurs.

*Tetrahydroxytriphenylmethane*,  $CHPh[C_6H_3(OH)_2]_2$ .—Resorcinolbenzein, when acted on by reducing agents, undergoes a change similar to phenolbenzein, and gives tetrahydroxytriphenylmethane, which crystallises from alcohol in colourless needles (m. p.  $= 171^\circ$ ). It is sparingly soluble in water, easily soluble in alcohol, ether, and glacial acetic acid. It dissolves in alkalis to a colourless solution, and is reprecipitated in the crystalline state on the addition of an acid; on oxidation or on heating, it is reconverted into resorcinolbenzein; its alkaline solution is coloured yellowish-brown by potassium ferricyanide.

*Tetrabromoresorcinolbenzein*,  $C_{18}H_6Br_4O_6$ , is obtained by passing bromine vapour into an alcoholic solution of resorcinolbenzein, or better, by adding the calculated amount of bromine dissolved in glacial acetic acid. It forms a fiery red powder, which is insoluble in water, and only very sparingly soluble in alcohol, glacial acetic acid, and other solvents, and could not therefore be obtained in the crystalline state. Its alkaline salts are sparingly soluble in water, but easily in alcohol, yielding a pomegranate-red solution

similar to those of the eosin salts; this solution dyes silk and wool like eosin; its spectrum also greatly resembles that of the latter body. An attempt to obtain an acetyl compound of resorcinolbenzein was unsuccessful. Resorcinolbenzein is not taken up by acids, or by alkaline sulphites, in this respect differing from phenolbenzein.

As in the case of phenol and resorcinol, 1 mol. of benzotrichloride combines with 2 mols. of the other phenols, forming dyestuffs belonging to the triphenylmethane group. Those with the cresols, pyrocatechol, quinol, orcinol, and  $\beta$ -naphthol are yellow or yellowish-red bodies; that with pyrogallol, on the other hand, is blue; and that with  $\alpha$ -naphthol green. The great similarity of the compounds of the phenols with benzotrichloride on the one hand, and with phthalic acid on the other, appears to show that the latter are like the former, derivatives of triphenylmethane, thus:—



T. C.

**A Product obtained by the Action of Aqua Regia on Orcinol.** By S. REYMANN (*Ber.*, 13, 809—811).—This body is the chlorine substitution-product of Liebermann's colouring matter  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_6$ , obtained by the action of nitrous acid on orcinol. It consists of  $\text{C}_{21}\text{H}_{17}\text{ClN}_2\text{O}_6$ . Resorcinol, under similar conditions, yields two bodies, of which one is probably analogous in composition to the above, whilst the other contains no chlorine. The first one dissolves in alkalis, with a pure blue colour.

G. T. A.

**Oxidation of Benzoic and Acetic Carbinols.** By A. BREUER and T. ZINCKE (*Ber.*, 13, 635—641).—*Benzoylcarbinol*,  $\text{Ph.CO.CH}_2\text{OH}$ , gives benzoic aldehyde and benzoic acid when oxidised with silver solution (compare *ibid.*, 10, 1486; this Journal, 1878, Abstr., 223). By oxidation with copper sulphate and soda, however, it gives chiefly mandelic acid,  $\text{CPhH}(\text{OH}).\text{COOH}$  (m. p. 115—118°), together with small quantities of benzoylformic and benzoic acids. The formation of mandelic acid is represented as follows:—(1.)  $\text{Ph.CO.CH}_2\text{OH} = \text{Ph.COH} + \text{H.CO.H}$ . (2.)  $\text{Ph.COH} + \text{H.CO.H} = \text{Ph.CH}(\text{OH}).\text{CO.H}$ . The mandelic aldehyde is then oxidised to the corresponding acid by the copper sulphate. The melting point of methyl mandelate is 48°, and not 114°, as stated by Naquet and Louguinine (*Annalen*, 139, 301). For the determination of the products of oxidation of acetylcarbinol, the acetate or benzoate must be employed, as the acetylcarbinol itself cannot be obtained in the pure state.

*Acetylcarbinol acetate*,  $\text{Me.CO.CH}_2.\text{OAc}$  (b. p. = 172°), was prepared by adding 5 parts of monochloracetone gradually to a warm solution of 8 parts of anhydrous potassium acetate in 20 parts of alcohol. Ethyl acetate and a liquid boiling at 125—135° (mesityl oxide?) are also obtained at the same time. Acetylcarbinol acetate thus prepared agrees in every respect with that obtained by Henry (*Ber.*, 5, 966).



*Acetylcarbinol benzoate*,  $\text{Me.CO.CH}_2.\text{OBz}$ , was obtained like the acetate. It is a slightly yellow aromatic liquid (b. p. =  $189-190^\circ$  at 50–60 mm.;  $200-201^\circ$  at 80–90 mm.; and  $263-264^\circ$  at the ordinary pressure, in the last case with slight decomposition), which on long standing becomes crystalline, forming colourless needles (m. p.  $24^\circ$ ). These are easily soluble in ether, alcohol, &c.; but only sparingly soluble in cold water, more easily in hot.

Acetylcarbinol acetate on oxidation with soda and copper sulphate, gives lactic acid, together with a small quantity of pyrotartaric acid. It is probable that all compounds containing the group  $-\text{CO.CH}_2.\text{OH}$  will, under similar circumstances, give bodies with the group  $-\text{CH}(\text{OH}).\text{COH}$ .  
T. C.

**Pinacones and Pinacolins.** By W. THÖRNER and T. ZINCKM (*Ber.*, 13, 641–647).—A continuation of the authors' previous work on this subject (*Ber.*, 10, 1473; 11, 65, 1396, 1988; this Journal, Abstr., 1878, 223, 425, 874; and 1879, 317). From their results, they draw the following general conclusions:—All ketone-pinacones, when exposed to a high temperature, split up into a ketone and an iso-alcohol. With those pinacones containing a benzene radicle, this decomposition takes place easily; whereas in the case of those containing paraffin radicles, it only occurs with considerable difficulty. To the pinacones there correspond two kinds of pinacolins, of which the one ( $\beta$ ) can be easily obtained; whilst the other ( $\alpha$ ) is only obtained with difficulty, and then only from those pinacones which contain a benzene radicle. Both pinacolins can also be obtained directly from the ketones, although up to the present the  $\alpha$ -pinacolin has only been got from purely aromatic ketones; those on the other hand, which, like acetophenol, contain also paraffin radicles, give only  $\beta$ -pinacolins, and that not directly in the case of those ketones which belong entirely to the paraffin series. No pinacone is known which partakes at the same time of the character of a true diatomic alcohol.  
T. C.

**Crystalline Form of Benzyl Orthothioformate.** By M. DENNSTEDT (*Ber.*, 13, 238–240).—This substance crystallises in the rhombic system  $a : b : c = 0.9978 : 1 : 0.9900$ ; observed forms, 100, 010, 001, 011, 101, 021, 201.  
C. E. G.

**Occurrence of Vanillin in Raw Sugars.** By E. O. v. LIPPMAHN (*Ber.*, 13, 662–665).—The author, like Scheibler (*Ber.*, 13, 335; this vol., 467), finds that vanillin occurs in certain kinds of raw sugar.  
T. C.

**Dioxybenzophenone.** By W. STAEDEL and E. SAUER (*Ber.*, 13, 836).— $\beta$ -*dioxybenzophenone*,  $\text{C}_{13}\text{H}_{10}\text{O}_3$ , is prepared by the action of dilute sulphuric acid and potassium nitrite on flavine obtained by the reduction of dinitrobenzophenone (m. p.  $148^\circ$ ). It crystallises in white needles (m. p.  $161^\circ$ ), which are more soluble in water than the crystals of  $\alpha$ -dioxybenzophenone (*Ber.*, 11, 746). The ethereal salt,  $\text{C}_{13}\text{H}_9\text{O}_3\text{Bz}_2$ , which is formed by the action of benzoic chloride on  $\beta$ -dioxybenzophenone, is deposited from an alcoholic solution in silky leaves (m. p.  $101^\circ$ ). The diacetic compound,  $\text{C}_{13}\text{H}_9\text{O}_3\text{Ac}_2$  (m. p.  $90^\circ$ ),

also crystallises in plates.  $\beta$ -dioxymetaphenone is decomposed by fusion with potash, forming phenol and paroxybenzoic acid.

W. C. W.

**Nitrobenzoic Acids.** By A. CLAUS (*Ber.*, 13, 891—896).—A considerable quantity of Fittica's "lemon yellow" mononitrobenzoic acid (*Ber.*, 11, 1207, and this Journal, Abstr., 1878, 980) was prepared, and was shown to possess no constant melting point. By repeated fractional recrystallisation, it was separated into meta- and ortho-nitrobenzoic acids.

W. C. W.

**Metaparanitrobenzoic Acid by Nitration of Paranitrobenzoic Acid.** By A. CLAUS and W. HALBERSTADT (*Ber.*, 13, 815—817).—By the action of a mixture of 1 part of fuming nitric acid and 2 parts of fuming sulphuric acid on paranitrobenzoic acid in a closed tube, the authors obtained a mixture of ortho- and meta-paranitrobenzoic acids. The two acids can be separated with some difficulty by means of the barium salts, that of the latter acid being more sparingly soluble.

Metaparanitrobenzoic acid melts at  $161^\circ$  (uncor.), is easily soluble in ether, alcohol, and hot water, but sparingly so in cold water. It crystallises in small colourless stellate groups, which contain no water of crystallisation. Its solution in hot water has an intensely bitter taste. It sublimes unchanged, but explodes when heated on platinum foil. The *barium* salt crystallises in white radiating masses, and contains  $4\text{H}_2\text{O}$ . The *calcium* salt consists of small white plates, becoming yellow at  $130^\circ$ , and losing 3 mols.  $\text{H}_2\text{O}$  at  $136^\circ$ . The *potassium*, *sodium*, and *ammonium* salts are very soluble, but have not been obtained in the crystalline state.

By heating paranitrobenzoic acid in closed tubes with bromine and water up to  $200^\circ$ , the authors have obtained a brominated compound; but whether this is brominated nitrobenzoic acid is doubtful.

G. T. A.

**Orthohydrazinbenzoic Acid.** By E. FISCHER (*Ber.*, 13, 679—682).—This acid, together with a small quantity of orthodiazobenzimide (m. p.  $144^\circ$ , *Zeits. f. Chem.*, 1867, 164), is obtained from anthranilic acid in a similar manner to phenylhydrazine. It crystallises from hot water in fine needles, which are much less soluble in alcohol and ether than in water. On oxidation, it behaves like the primary hydrazines, and is completely decomposed with evolution of gas by Fehling's solution, and by mercury and silver salts even in the cold. The *hydrochloride*,  $\text{C}_6\text{H}_4(\text{COOH})\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ , crystallises from hot water, in fine white needles, which are easily soluble in hot water, less soluble in alcohol, and almost insoluble in ether. The salts of orthohydrazinbenzoic acid are easily soluble, and its alkaline solution may be boiled for some time without any marked decomposition.

*Hydrazinbenzoic anhydride*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix}\rangle\text{NH}$ , is obtained by warming the acid with strong hydrochloric acid, or better by heating the acid alone at  $220$ — $230^\circ$  in an atmosphere of carbonic anhydride. It separates from alcohol in colourless compact crystals, which are sparingly soluble in water, alcohol, and ether. By careful heating, it

melts and sublimes in colourless needles, but is partially decomposed when rapidly heated. It no longer has basic properties, but dissolves in alkalis and decomposes carbonates. It is more stable towards oxidising agents than the ordinary hydrazine bases, and is not acted on by Fehling's solution or by mercuric salts. Silver nitrate throws down a white precipitate of the silver salt, consisting of fine needles, which are decomposed on boiling. The anhydride reduces ammoniacal silver solutions.

T. C.

**Anthranilic Acid from Orthonitrotoluene.** By P. GREIFF (*Ber.*, 13, 288—290).—The presence of the nitro-group in the ortho-position in orthonitrotoluene appears to render the methyl-group less susceptible of change. Thus Wachendorff (*Annalen*, 185, 259) found that the latter was unaffected by chlorine or bromine even at a high temperature, these elements attacking the benzene nucleus. Amongst the products of the action of bromine, he noticed a body soluble in alkalis, which he erroneously took to be dibromonitrotoluene. On repeating Wachendorff's experiment, the author finds this body to be *parametabromorthoamidobenzoic acid*,  $C_6H_4Br_2(NH_2).COOH$ , isomeric with dibromanthranilic acid and with dibromnitrotoluene. A singular interchange of hydrogen and oxygen between the methyl and nitro-groups takes place during the reaction, which hence may be used for preparing anthranilic acid. This is effected by allowing 2 mols. of bromine to drop gradually into orthonitrotoluene heated at  $170^\circ$ . Hydrobromic acid is rapidly given off, and so much heat developed that external heating is unnecessary when the weight of substance exceeds 200 grams. From the solid mass obtained on cooling, the acid may be separated by sodium carbonate; the yellowish-white mass deposited on adding an acid may be converted into barium salt by boiling with barium carbonate, and the acid precipitated from the filtered solution, crystallised from alcohol (m. p.  $225^\circ$ ). By treating its alkaline solution with sodium amalgam in the cold, anthranilic (ortho-amidobenzoic) acid is easily formed (m. p.  $145^\circ$ ): this yields salicylic acid when treated with nitrous acid, and aniline when distilled with lime.

The brominated acid is probably identical with Hübner's dibromanthranilic acid (m. p.  $225^\circ$ ) from dibromobenzoic acid; an isomeride (m. p.  $196^\circ$ ) has been similarly prepared by Hübner (*Ber.*, 10, 1706).

Wachendorff did not obtain acid bodies by brominating para- and meta-nitrotoluene.

In the above reaction, nitrobenzyl bromide is perhaps first formed: the passage of this into anthranilic acid would then be analogous to the conversion of benzyl chloride into benzoic acid by the action of nitric acid. A similar oxidation of the methyl-group of toluidine occurs in the so-called nitrofuchsine-melt; and the formation of chlorinated bases when certain nitro-compounds are reduced by tin and hydrochloric acid, and that of dichloramidophenol by the action of hydrochloric acid on nitrosophenol, are also cases in point.

Ch. B.

**Aromatic Products of the Animal Body.** By R. BAUMANN (*Ber.*, 13, 279—285).—Hydroparacoumaric acid being the first, and under the conditions given by the author (*Ber.*, 12, 1452), the final

putrefaction product of tyrosine, putrefaction affords a convenient method of preparing it. 20 grams of tyrosine thus yield 12 grams of hydroparacoumaric acid. Salkowski has shown (*Ber.*, 13, 189) that when it occurs amongst the decomposition-products of albumin, it is also derived from previously-formed tyrosine.

The homologous parahydroxyphenylacetic acid is also generated during the digestion of albumin, and may be detected in the urine by evaporating 5—10 c.c. with hydrochloric acid to remove phenols, and extracting with ether. With Millon's reagent the ethereal extract gives the red colour characteristic of hydroxy-acids. The acid may be prepared by evaporating 25 litres of urine to  $1\frac{1}{2}$  litres, strongly acidifying with acetic acid and shaking with ether, a little alcohol being added to decompose the emulsion which frequently forms. The extract, freed from acetic acid, is again dissolved in water and exhausted with ether. The portion of this second extract, soluble in water, gives with basic lead acetate a precipitate of lead parahydroxyphenylacetate, from which the acid may be liberated by sulphuretted hydrogen, and purified by crystallisation from water and benzene (m. p.  $148^{\circ}$ ). About  $\frac{1}{2}$  gram of crude acid is thus obtained. Hydroparacoumaric acid (m. p.  $126$ — $127^{\circ}$ ) is occasionally obtained from the urine by the same process: it separates more slowly and incompletely from hot benzene than its homologue.

Parahydroxyphenylacetic acid might be supposed to owe its origin to an amido-acid,  $C_6H_5NO_2$ , homologous with tyrosine, especially since Schützenberger has detected numerous amido-acids of the fatty series amongst the decomposition-products of albumin; the author shows, however, that tyrosine alone is produced when horn-clippings are boiled with dilute sulphuric acid.

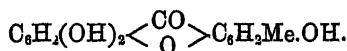
In order, if possible, to detect some of the transition-products between hydroparacoumaric acid and phenol (*Ber.*, 12, 1453), 5 grams of the former were administered to a man in whose urine hydroxy-acids and phenols were normally present only in minute quantities. On subsequently examining the urine, it was found that the greater part of the acid had been destroyed; a small part (.8 gram) was obtained unchanged; and a still smaller quantity had been converted into a phenol, obtained as an ethereal sulphate. Parahydroxyphenylacetic acid could not be detected.

That portion of the ethereal extract from urine, obtained as above described, which was sparingly soluble in water, contained oily acids which reacted with nitric acid like indole, and on prolonged contact with putrescent substance yielded a considerable amount of skatole, but no indole. These nitrogenous acids dissolve in hydrochloric acid, and are resinified when boiled with it. They are probably the sources of skatole and indole in the urine, and in decomposed albumin; since after either has been boiled with hydrochloric acid and the precipitated resins removed, the bases are no longer obtained by putrefaction: and putrescent albumin, not so far decomposed as to contain indole after being agitated with ether, does not yield indole on further putrefaction; whilst the ethereal extract, when neutralised with sodium carbonate and diluted with water, yields that base on standing in the incubator for six days.

Ch. B.

**History of Phenylacetamide.** By A. BERNTHSEN (*Ber.*, 13, 817).—Referring to Reimer's paper in *Ber.*, 13, 741, the author states that phenylacetamide (alphetoluylamide) was prepared by Weddige (Stædel's *Jahresb.*, 1873, 324), and by himself (*Annalen*, 184, 294 and 316) from benzyl cyanide. G. T. A.

**Phlobaphene.** By C. BÖTINGER (*Annalen*, 202, 269—287).—Phlobaphene is identical with the red substance (oak red), obtained by boiling quercitannic acid with dilute acids; it has the formula  $(C_{14}H_{10}O_6)_2 \cdot H_2O$ , and forms a reddish-brown powder insoluble in most of the ordinary solvents, but soluble to a considerable extent in solution of quercitannic acid; it is also soluble in aqueous alkalis, yielding a reddish-brown liquid, which absorbs oxygen. Acetic anhydride at  $140^\circ$  converts it into triacetylphlobaphene,  $C_{14}H_7O_6 \cdot 3Ac$ ; benzoic chloride at  $130^\circ$  gives tribenzoylphlobaphene,  $C_{14}H_7O_6 \cdot 3Bz$ . On heating with strong hydrochloric or hydriodic acid, phlobaphene loses a molecule of water and one of carbonic anhydride, and is converted into a brilliant black powder. This substance appears to be closely related to the body obtained by heating pyrogallol at  $160$ — $180^\circ$  with strong hydrochloric acid, which on analysis gives results agreeing with those for a mixture of the two pyrogallol ethers,  $C_6H_6O_3$  and  $C_6H_6O_4$ , and which also appears to be a tanning agent; the leather it produces is black. Schiff has shown (*Annalen*, 170, 43; this Journal, 1874, 270) that tannin is the anhydride of carboxylpyrogallol, and from the results given above phlobaphene may be regarded as the anhydride of methylpyrogallol and carboxylpyrogallol—



The author considers it probable that phlobaphene is the essential tanning agent in oak bark. A. J. G.

**Compounds of Phthalic Acid with Phenols.** By A. BANYER (*Annalen*, 202, 36—140).—In a former communication (this Journal, 31, 196), the author has described several compounds belonging to this category. In the introduction, a historical sketch is given of the views held as regards the constitution of these compounds, which finally led to the adoption of those given in this Journal (36, 636).

I. *Triphenylmethane Group.*—*Derivatives of Diphenylphthalide.*—*Diphenylphthalide*,  $Ph_2C < \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > C$ , was prepared according to Friedel and Crafts' method (*Compt. rend.*, 11th June, 1877); it crystallises in needles, m. p.  $112^\circ$ , and dissolves in concentrated sulphuric acid, forming a greenish-yellow solution, becoming violet when heated.

*Triphenylcarbinolorthocarboxylic acid*,  $C(OH)Ph_2.C_6H_4.COOH$ —Its potassium salt is formed by treating diphenyl phthalide with alcoholic potash; the free acid cannot be obtained as it is immediately resolved into diphenylphthalide. It corresponds with the benzeno-ortho-alcoholic acid described by Hessert (*ibid.*, 34, 419).

*Triphenylmethanecarboxylic acid*,  $CHPh_2.C_6H_4.COOH$ , is prepared by reducing the sodium salt of the above acid with zinc-dust; its forma-

tion is expressed as follows:  $\text{C}(\text{OH})\text{Ph}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{H}_2 = \text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOH} + \text{H}_2\text{O}$ .

Acids precipitate it from the solutions of its salts, and it crystallises from alcohol in large needles (m. p. 155—157°). On exposure to the air or by treatment with chromic acid, it is converted into diphenylphthalide. Triphenylmethanecarboxylic acid is insoluble in water, easily soluble in ether and glacial acetic acid, dilute alkalis and alkaline carbonates dissolve it; it is soluble in hot concentrated alkalis, and on cooling the salt separates out. When heated with baryta, it yields phenylmethane, which crystallises in needles (m. p. 92·5°), and on oxidation yields triphenylcarbinol (m. p. 159°), which was converted into rosaniline by E. and O. Fischer's method (*ibid.*, 34, 384).

## II. Anthracene Derivatives of Diphenylphthalide. By A. Schellinger

(*Annalen*, 202, 54—65).—Phenylanthranol,  $\text{Ph}\cdot\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}\cdot\text{OH}$ , is

obtained by treating triphenylmethanecarboxylic acid with concentrated sulphuric acid, phosphorus pentachloride, or phosphoric anhydride. It crystallises from alcohol in yellow needles (m. p. 141—144°); when strongly heated a portion distils, whilst the greater portion carbonises. Hot alcohol, light petroleum, and acetone dissolve it, forming yellow solutions, from which it separates on cooling. It is easily soluble in ether, forming a greenish-yellow fluorescent solution. Cold dilute alkalis or alkaline carbonates do not dissolve it, whereas on warming they dissolve it, forming yellow solutions, from which acids separate a yellow flocculent precipitate. Its composition and properties show it to be a phenyl derivative of the anthranol described by Liebermann and Topf (*Ber.*, 9, 1201).

Monacetophenylanthranol,  $\text{C}_{20}\text{H}_{13}\cdot\text{O}\cdot\text{Ac}$ , is prepared by heating phenylanthranol with acetic anhydride; alcohol, ether, benzene, and acetone dissolve it easily, forming blue fluorescent solutions. Concentrated sulphuric acid decomposes it into its constituents, whereas it is but slightly acted on by dilute alkalis or alkaline carbonates. From alcohol, it crystallises in tufts of yellow needles (m. p. 165—166°).

Phenylloxanthranol,  $\text{Ph}(\text{OH})\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CO}$ , is prepared by oxidising phenylanthranol in glacial acetic acid solution with potassium dichromate. On diluting the solution with water, it separates as a white curdy precipitate. It is insoluble in water, but alcohol and similar solvents dissolve it easily; water precipitates it from its alcoholic solution in colourless shining leaflets. It crystallises from glacial acetic acid in colourless, acute, rhombic plates, which redden on exposure to the air, and melt at 208°. It dissolves in concentrated sulphuric acid with an intense purple-red colour; when heated, it becomes blue, the solution producing a strong absorption-band between the blue and green, and two weaker ones in the yellow. When heated further, it becomes violet; these colorations are probably due to the formation of sulphonic acids. It is related to phenylanthranol in the same way that anthraquinol is to anthranol. A monacetyl derivative

seems to be produced when phenyloxanthranol is heated with acetic anhydride in sealed tubes at  $180^{\circ}$ .

*Phenylanthracene*,  $\text{PhC} \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{CH}$ , is prepared by heating phenyl-

anthranol, diphenylphthalide, on triphenylmethanecarboxylic acid with zinc-dust. Alcohol, ether, benzene, carbon bisulphide, and chloroform dissolve it easily on warming, forming solutions having a blue fluorescence, and from which it separates in yellow leaflets (m. p.  $152-153^{\circ}$ ) on cooling. Concentrated sulphuric acid dissolves it forming a yellow solution, which, on heating, becomes brown. When heated, phenylanthracene distils. Like anthracene, it forms a compound with picric acid, and on oxidation yields phenyloxanthranol.

*Phenylanthracene dihydride*,  $\text{C}_{20}\text{H}_{18}$ , may be prepared by reducing phenylanthracene with hydriodic acid, or by the action of the same reagent on phenyloxanthranol at  $150-170^{\circ}$ , or on triphenylmethanecarboxylic acid at  $180-200^{\circ}$ . The product of these reactions is extracted by ether, shaken up with sulphurous acid, and the ethereal solution evaporated. By dissolving the residue in alcohol and evaporating, it is obtained as an oil, which solidifies to a crystalline mass (m. p.  $120-120.5^{\circ}$ ); it may be distilled without decomposition. Its properties are similar to those of anthracene dihydride (Graebe and Liebermann, *Annalen*, Supp. 7, 265), save that it forms a compound with picric acid, which may be due to the presence of a little phenylanthracene. It dissolves in the same solvents as phenylanthracene, the solutions exhibiting a blue fluorescence. On oxidation it yields phenyloxanthranol. By the further action of hydriodic acid, higher hydrides are formed.

By treating the solution of phenyloxanthranol in concentrated sulphuric acid with benzene, a compound,  $\text{C}_{26}\text{H}_{14}\text{O}$ , is formed, thus:  $-\text{C}_{20}\text{H}_{18}\text{O}_2 + \text{C}_6\text{H}_6 = \text{C}_{26}\text{H}_{14}\text{O}_2 + \text{H}_2\text{O}$ . It crystallises from alcohol and benzene in colourless crystals. Phenol forms a similar compound.

III. *Conversion of Diphenylphthalide into Phenolphthalein*.—This conversion was effected, as has been stated (this Journal, 36, 636), by the replacement of the nitro-groups in dinitrodiphenylphthalide by two hydroxyl groups.

*Dinitrodiphenylphthalide*,  $\text{C}_{20}\text{H}_{12}(\text{NO}_2)_2\text{O}$ , is prepared by dissolving the phthalide in concentrated nitric acid: water precipitates it from this solution in amorphous flocks. It separates from hot methyl alcohol in the form of oily drops, which solidify and melt at  $75-95^{\circ}$ . It is probably a mixture of isomeric nitro-derivatives. When heated with concentrated sulphuric acid it yields a body resembling alizarin.

*Diamidodiphenylphthalide*,  $\text{C}_6\text{H}_4 : \text{CO} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} \text{C}(\text{C}_6\text{H}_4.\text{NH}_2)_2$ , is prepared

by the reduction of the nitro-derivative, and the free base precipitated from its salts by sodium carbonate. It crystallises from alcohol in thick lustrous plates, melting at  $179-180^{\circ}$ . The alcoholic mother-liquors on evaporation yield a small quantity of another body in the form of crusts melting at  $205^{\circ}$ . The chief product, viz., that melting

at 179—180°, is easily soluble in alcohol and ether (in the crystalline state less soluble than when amorphous); it is sparingly soluble in benzene and water, and insoluble in light petroleum. When heated with concentrated sulphuric acid, it gives anthraquinol. It dissolves in glacial acetic acid with reddish-violet colour, but its solution in hydrochloric acid is colourless.

When heated with methyl alcohol and hydrochloric acid at 180°, it gives a green colouring matter, apparently identical with that obtained by O. Fischer by the action of dimethylaniline on phthalyl chloride, and is probably tetramethyldiamidodiphenylphthalide,  $C_{20}H_{12}O_2(NMe_2)_2$ .

Nitrous acid converts the diamidophthalide into phenolphthalein.

IV. *Triphenylmethane Derivatives of Phenolphthalein*.—The method of preparing phenolphthalein by the action of sulphuric acid on phenol and phthalic anhydride has been already described (*Ber.*, 9, 1230); it may also be prepared by heating  $1\frac{1}{2}$  parts of phthalic anhydride, 2 of phenol, and  $2\frac{1}{2}$  of tin chloride at 115—120°. The hot melt so obtained is poured into water, and washed with hot water until all phenol is removed. The residue is then treated with soda, and the phthalein precipitated from the violet solution by means of acetic acid and a little hydrochloric acid; it separates out as a yellowish-white sandy powder, which is purified by precipitating its alcoholic solution by water, part separates out in a resinous form, after removal of which the phthalein separates out in large crystals. These crystals, which may also be obtained by dissolving it in water or hydrochloric acid at 150—200°, are lance-shaped, and the measurements show them to be triclinic. Phthalein is easily soluble in alcohol, methyl alcohol, or glacial acetic acid, and crystallises from these solutions in scales. Ether dissolves amorphous phthalein easily, but when crystallised it is only sparingly soluble. It melts at 250—253°, forming a colourless liquid, which solidifies to a vitreous mass at 217—210°. By stronger heat, it is decomposed, with liberation of phenol. Concentrated sulphuric acid dissolves it, forming a yellow-red solution, from which it is precipitated by water. Heated with sulphuric acid at 100°, a sulphonic acid is produced, whereas at 200°, oxyanthraquinol is formed. Nitric acid yields a nitro-derivative; no dinitro-derivative has been obtained.

Phenolphthalein forms unstable salts; caustic alkalis and alkaline carbonates dissolve it, forming reddish-violet solutions, which have an absorption-spectrum between the green and yellow. These solutions are decolorised by an excess of caustic alkali, and the colour restored by addition of acid, showing that phenolphthalein might be used in alkalimetry. It is also dissolved by ammonia; on boiling, the ammonia is expelled and the phthalein separates out. Alum and copper salts precipitate unaltered phthalein from its alkaline solutions. The silver salt is obtained as a violet amorphous precipitate, which on heating becomes crystalline and then decomposes.

*Diacetoxyphenolphthalein*,  $C_{20}H_{12}O_4(AC)_2$ , has been already described (*loc. cit.*).

The methyl salt of phenolphthalein has been obtained by heating 1 part of phthalein, 0.5 of potash, and 3 of methyl iodide, with alcohol at 100°; it is a crystalline compound.



*Chloride of phenolphthalein or dichlorodiphenylphthalide*,  $C_{20}H_{12}O_2Cl_2$ .—To the description (*loc. cit.*) already given of this body is added that when boiled with concentrated sulphuric acid, it yields a compound, apparently a dichloro-anthraquinol, which when fused with soda yields alizarin.

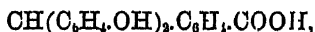
*Dichlorodiphenylcarbinolcarboxylic acid*.—Its potassium compound is produced by the action of alcoholic potash on dichlorodiphenylphthalide. The acid cannot be prepared, as the dichlorophthalide separates out on acidifying its alkaline solution.

Phenolphthalein dissolves in concentrated sulphuric acid, and if the solution is heated on a water-bath, sulphonic acids are formed; when heated strongly, decomposition takes place, phthalic anhydride and phenolsulphonic acid being formed, which react at  $200^\circ$  to form oxy- and erythroxy-anthraquinone.

*Tetrabromophenolphthalein*,  $C_{20}H_8Br_4O_4$ .—The preparation of this body has already been described (*loc. cit.*); it crystallises in short prisms, melting at  $220$ – $230^\circ$ . Its behaviour with caustic alkalis is similar to that of phenolphthalein; it is, however, a stronger acid than this body, and its solutions in alkalis have a deeper violet colour. Alum and copper salts precipitate the bromophthalein from its solutions in alkalis; lead salts give a white lead compound, and silver salts a bluish-violet precipitate of a silver compound. It dissolves in concentrated sulphuric acid with a light red colour, and is reprecipitated by water; when strongly heated with sulphuric acid, it gives dibromoxy-anthraquinone. Oxidising agents, such as nitric and chromic acids, form violet solutions containing a quinone. By the action of nitrous acid, part of the bromine is replaced by nitro-groups.

*Diacetotetrabromophenolphthalein*,  $C_{20}H_8Br_4O_4Ac_2$ , obtained by the action of acetic anhydride on tetrabromophthalein, crystallises from alcohol in globular crystalline masses (m. p.  $134^\circ$ ); when carefully heated it may be distilled. With sulphuric acid, it behaves similarly to the bromophthalein.

*Phenolphthalin, a dioxytriphenylmethanecarboxylic acid*,



is prepared from phenolphthalein in the same way as triphenylmethanecarboxylic acid is from diphenylphthalide. It crystallises from water and alcohol in concentrically grouped needles (m. p.  $225^\circ$ ), which are more soluble in water than phthalein. It is unacted on by zinc and soda, also by zinc and hydrochloric acid in presence of alcohol. Phosphorus and hydriodic acid yield resinous products, whereas with sodium amalgam, in presence of an acid, it forms phenolphthalol. The phthalin has marked acid properties; it dissolves barium carbonate, and gives colourless solutions with alkalis, which are coloured red by potassium ferricyanide and permanganate, owing to the formation of phthalein. The aqueous solutions of the phthalin give a colourless flocculent precipitate with lead acetate; its ammoniacal solution, freed from excess of ammonia, gives a blue precipitate with copper salts, and a white flocculent precipitate with silver nitrate, the latter is soluble in excess of ammonia. With sulphuric acid, the phthalin yields the following characteristic reaction; it dissolves forming a

reddish-yellow solution and on addition of water greenish-yellow flocks of phthalidin separate out. The solution in sulphuric acid gives a dark green when manganese dioxide is added to it, and the solution after diluting with water, yields phthalidein on extracting it with ether.

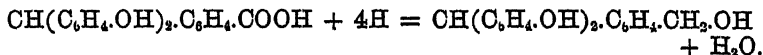
*Diacetophenolphthalin*,  $C_{24}H_{20}O_6$ , crystallises from alcohol in colourless needles (m. p.  $146^\circ$ ). Glacial acetic acid dissolves it largely; it is sparingly soluble in cold, more easily in warm alcohol.

*Chloride of Phenolphthalin*,  $\alpha$ -*Dichlorotriphenylmethanecarboxylic Acid*,  $CH(C_6H_4Cl)_2.C_6H_4.COOH$ .—This body cannot be prepared by the direct action of phosphorus pentachloride on phenolphthalin, but is obtained by reducing the chloride of the phthalein with hydriodic acid, or zinc-dust and soda. Prepared by the former method, and crystallised from glacial acetic acid, it forms colourless crystals (m. p.  $195^\circ$ ); whilst by the latter method, and crystallisation from alcohol, it is obtained in fern-like masses of needles (m. p.  $205-206^\circ$ ). Alcohol, ether, and acetone dissolve it easily; it crystallises from alcohol in six-sided tablets. It dissolves easily in alkaline carbonates and caustic alkalis, forming salts which are sparingly soluble in alkaline solutions. Warm concentrated sulphuric acid dissolves it, forming yellow solutions, which rapidly change to green, blue, and finally violet. This latter colour is produced instantaneously on adding potassium dichromate, and is due to the formation of dichlorophenyl-anthranol.

*Tetrabromophenolphthalin*,  $CH(C_6H_4Br_2.OH).C_6H_4.COOH$ , may be prepared like the phthalin by reduction of the brominated phthalein, or better still by treating the phthalin in acetic acid solution with bromine. It crystallises in compact needles (m. p.  $205^\circ$ ); is easily soluble in alcohol, methyl alcohol, acetone, glacial acetic acid, carbon bisulphide, and ether; it is soluble in warm, and sparingly in cold benzene, and also sparingly soluble in chloroform. It dissolves slowly in concentrated sulphuric acid with reddish-yellow colour, which becomes green owing to the formation of tetrabromophthalidin.

*Diacetyltetrabromophthalin*,  $C_{20}H_{12}Br_4O_4Ac_2$ , crystallises in stellate-grouped needles, melting at  $165-166^\circ$ .

*Phenolphthalol*,  $C_{24}H_{18}O_3$ , is prepared by reducing the phthalin with sodium-amalgam and acetic acid until the solution, after acidifying with sulphuric acid, ceases to yield a fluorescent solution on extraction with ether. It crystallises from dilute acetic acid in large prismatic crystals, and from water, in which it is sparingly soluble, in lance-shaped crystals. Alcohol, ether, and acetone dissolve it easily, whilst it is insoluble in benzene or chloroform. It melts at  $190^\circ$ , and may be distilled. Its alkaline solutions, which are colourless, are oxidised by potassium ferricyanide, the phthalein being formed. Its formation from the phthalin is expressed as follows:—



It is therefore an alcohol, and, like aromatic alcohols when treated with concentrated sulphuric acid, it yields condensation-products. The existence in it of three hydroxyl-groups is shown by the formation of

a triacetyl derivative,  $C_{20}H_{15}O_7\bar{A}c_3$ , a vitreous mass (m. p.  $40^\circ$ ) capable of being distilled. It is insoluble in water, but soluble in alcohol, ether, and benzene.

V. *Phenylanthracene-derivatives of Phenolphthalein*.—*Phenolphthalidin*,  $\alpha$ -dioxypyphenylanthranol,  $C_{20}H_{14}O_3$ . The production of this body has already been described (*Ber.*, 9, 1234). By long-continued action of concentrated sulphuric acid, it is converted into sulphonic acids. Heated with sulphuric acid at  $120^\circ$ , it forms a dark-green solution which, on boiling, becomes red. Its formation is similar to that of phenylanthranol from triphenylmethanecarboxylic acid, and to it is

assigned the constitutional formula:  $OH.C \begin{array}{c} \swarrow C_6H_4 \searrow \\ \nwarrow C_6H_3.OH \end{array} C.C_6H_4.OH$ .

*Tetrabromophthalidin*,  $OH.C \begin{array}{c} \swarrow C_6H_4 \searrow \\ \nwarrow C_6HBr_3.OH \end{array} C.C_6H_2Br_2.OH$ . This body is

produced in a similar manner to the above (*loc. cit.*). It dissolves in potash solution with a yellow colour, and on warming, the potassium salt separates out in green crystals. It is soluble in concentrated sulphuric acid with a green colour, which changes to blue when heated at  $130$ — $140^\circ$ , owing to the formation of tetrabromophthalidein. This latter body is also formed by the action of oxidising agents. Bromine acts on it, forming a compound which is decomposed by water into bromophthalidein.

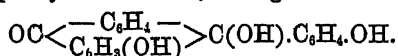
*Diacetotetrabromophthalidin*,  $C_{20}H_{12}Br_4O_5\bar{A}c_2$ , crystallises from glacial acetic acid in long hair-like needles. It is easily soluble in chloroform, benzene, and carbon bisulphide, forming a green fluorescent solution; water, alcohol, and glacial acetic acid dissolve it but sparingly. It melts at  $256^\circ$ ; when heated above its melting point it yields bromophenol.

*Phenolphthalidin Chloride*,  $\alpha$ -Dichlorophenylanthranol,  $C_{20}H_{12}Cl_2O$ .—It cannot be prepared by the action of phosphorus pentachloride on the phthalidin, but is obtained by reducing the phthalidein chloride with zinc and acetic acid, and is precipitated by water from the filtered solution as a yellow powder; it melts at about  $170^\circ$ , and may be distilled in small quantities. Alcohol and glacial acetic acid dissolve it sparingly, and it crystallises from these solutions in needles. With ether or acetone, it forms a bluish-green fluorescent solution, and it is easily soluble in benzene and carbon bisulphide. Concentrated sulphuric acid dissolves it, forming a reddish-yellow solution, from which water precipitates it. Bromine and oxidising agents convert it into the phthalidein chloride.

*Phenolhydrophthalidin chloride*,  $OH.HC \begin{array}{c} \swarrow C_6H_4 \searrow \\ \nwarrow C_6H_3Cl \end{array} CH.C_6H_4Cl$ , is obtained by the reduction of an alcoholic solution of phthalidin chloride with sodium-amalgam. It is easily soluble in ether, acetone, chloroform, and carbon bisulphide, sparingly in cold alcohol, methyl alcohol, and glacial acetic acid, but more easily when warm. It melts at  $56^\circ$ , and may be sublimed. By the action of concentrated sulphuric

acid, it forms condensation-products, dissolving with a yellow, then red coloration; from this solution, ether extracts a body differing from the phthalideïn chloride. Phenolphthaleidin is obtained by reducing the phthalideïn with zinc-dust and soda, or its alcoholic solution by zinc and hydrochloric acid. It cannot be obtained in a crystalline state; concentrated sulphuric acid converts it into a red condensation-product, and it is oxidised by potassium permanganate to the phthalideïn. Bromine converts it into the tetrabromophthalideïn. Sodium-amalgam and acetic acid reduce it to the phthalol.

*Phenolphthalidem*, *tetrabromophthalideïn*, and their derivatives have already been described (*ibid.*, 1235—1238). These compounds which are formed by the oxidation of the corresponding phthalidins, the author regards as derived from phenyloxanthranol; phenolphthalideïn being dioxyphenyloxanthranol, having the formula—



It contains three hydroxyl-groups, one of which is, as in the case of phenyloxanthranol, with difficulty acted upon by acetic anhydride.

VI. *Action of Ammonia on Phenolphthaleïn and its Derivatives.* By J. B. Burkhardt (*Annalen*, 202, 111—135).—The results of the action of ammonia on phenolphthaleïn, viz., the formation of diimidophenolphthaleïn, &c., have been described in this Journal (34, 866).

Ammonia has no action on phenolphthalin; the brominated derivative, it decomposes at 160—200°, forming bromophenol. It reacts with the phthalidin, forming the phthalideïn, which latter is reduced by alcoholic ammonia, whereas by aqueous ammonia it is converted into a brown insoluble body. The tetrabromophthalidin is decomposed by ammonia at 200° into bromophenol.

By the action of alcoholic or aqueous ammonia at 150—160° on the phenol compounds of phenolphthalideïn (*Ber.*, 9, 1237), a body is obtained crystallising from a mixture of acetone and water in pale yellow needles (m. p. 260°), which are easily soluble in methyl and ethyl alcohols, but sparingly soluble in chloroform, benzene, and carbon bisulphide. It has no basic properties; its solution in alkalis is colourless, whereas it dissolves in concentrated sulphuric acid with a blue colour. Its composition appears to be  $C_{20}H_{18}NO_3$ .

VII. *Oxidation of Tetrabromophenolphthaleïn.* By C. Schraube (*Annalen*, 202, 121—126).—An account of the formation of the bromoquinone to which the constitutional formula,  $<\overline{C_6H_2Br_2}>O_2$ , is attributed, has already appeared in this Journal (34, 869).

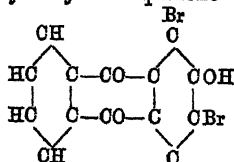
VIII. *Fusion of Phthaleïn and Phthalidin Derivatives with Potash.* By J. B. Burkhardt (*Annalen*, 202, 126—135).—Phenolphthaleïn when fused with potash yields dioxybenzophenone (*ibid.*, 34, 886); the phthalidin and phthalideïn yield the same product. The phthalin is acted on by potash at high temperatures only, and does not yield a dioxybenzophenone.

*Tetrabromodioxorybenzophenone*,  $CO(C_6H_2Br_2.OH)_2$ , is obtained by

treating the alcoholic solution of dioxybenzophenone with bromine; it is insoluble in water, chloroform, and carbon bisulphide, and sparingly soluble in alcohol, glacial acetic acid, methyl alcohol, and acetone. It crystallises in long needles or prisms (m. p. 213—214°), and may be distilled without decomposition. Alkalis dissolve it, forming colourless solutions. When fused with potash it yields a phenol-like compound, which is coloured green by ferric chloride; the tetrabromophthalein yields the same body. The existence of two hydroxyl groups in bromodioxyphenone is shown by the analysis of its acetyl-derivative and of its barium salt, obtained by treating its ammoniacal solution with barium chloride.

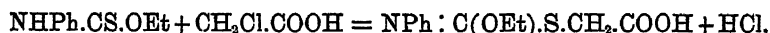
*Dioxybenzhydrol*.—This unstable body appears to be formed by the reduction of an aqueous solution of dioxybenzophenone by sodium amalgam. Since it cannot be obtained in the pure state, the solution after reduction is acidified and the product treated at once with acetic anhydride. Thus a compound is obtained, apparently tetracetodioxybenzhydrol,  $(C_6H_4.OAc)_2HC.CH(C_6H_4.OAc)_2$ . It is insoluble in water and light petroleum, easily soluble in hot alcohol and benzene. When heated, it is decomposed. Its dark-red solution in concentrated sulphuric acid exhibits thick absorption-bands between the blue and green, and when heated assumes a brownish-red tint. It is decomposed by boiling potash.

IX. *Formation of Oryanthraquinone from Phenolphthalein*.—An account of this has been already given (*Ber.*, 7, 968). Further, the formation of dibromoxyanthraquinone from tetrabromophenolphthalein, and its conversion into alizarin, has been described by the author (*ibid.*, 9, 1231). Dibromophenol, which is formed at the same time, may be prepared by distilling the tetrabromophthalein with concentrated sulphuric acid, diluting the distillate with water, and extracting with ether. The quinone is removed from the ethereal solution by means of lead acetate, and thus a dibromophenol is obtained melting at 55—56°, differing from 1.2.4 dibromophenol, which melts at 40°. Fraude (this Journal, 36, 634) has shown that orthocresolphthalein yields only a dibromo-derivative; from which the author concludes that the methyl-group in orthocresolphthalein occupies the position which the second bromine atom takes in tetrabromophenolphthalein. Again, Fraude has obtained from orthocresolphthalein a bromomethylhydroxyanthraquinone, yielding methylalizarin. Therefore the bromine atom in this quinone is in juxtaposition to the hydroxyl-group, and hence in tetrabromophenolphthalein both the bromine atoms are next to the hydroxyl-groups. So dibromophenol had the constitution  $C_6H_3OH.Br_2$  [1.2.6], and dibromhydroxyanthraquinone—

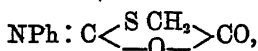


**Phenylthiocarbimide-glycollide.** By C. LIEBERMANN and M. VOELTZKOW (*Ber.*, 13, 276—279).—The experiments of Liebermann and Lange (*Ber.*, 12, 1588) have shown that in thiohydantoin and its derivatives, which by decomposition easily yield thioglycollic acid,  $\text{HS.CH}_2\text{COOH}$ , the residue  $-\text{CH}_2\text{COOH}$  must be directly united with the sulphur, and not with the nitrogen; and also that in the conversion of thiocarbimide into thiohydantoin, the sulphur plays the same peculiar part that it does in the formation of the alkylated thiamides of Wallach, Bernthsen, and others, and of Hofmann's chlorinated thiocarbimide.

To ascertain whether this reaction of sulphur is general, molecular weights of chloracetic acid and phenylthiourethane were heated together with a little absolute alcohol at  $160-170^\circ$ . The following reaction was expected to occur:—



but instead of this product the authors obtained a compound derived from it by elimination of alcohol, to which the constitution—



must be assigned. This body is soluble in alcohol and insoluble in cold water, but crystallises from boiling water in white plates (m. p.  $148^\circ$ ). It is identical with the compound,  $\text{C}_6\text{H}_7\text{NSO}_2$ , which Lange obtained by the action of hydrochloric acid on diphenylthiohydantoin.

On boiling with baryta-water, it is almost quantitatively decomposed as follows:—



It may therefore be regarded as an addition-product of phenylthiocarbimide with glycollide, and may be named phenylthiocarbimide-glycollide. It cannot be directly formed from these bodies, but is very easily produced when phenylthiocarbimide and chloracetic acid (or ethyl chloracetate) are heated together with a little alcohol at  $160-170^\circ$ . In this reaction, however, phenylthiourethane may be formed as an intermediate product: and in fact a different reaction appears to occur when ether is substituted for the alcohol.

An isomeride of this body, acetoxothiocarbimide, has been obtained by Hofmann. The two bodies have different characters: the constitutional difference between them is shown by the action of alkalis, whereby the latter is decomposed into oxythiocarbimide and acetic acid (*Ber.*, 12, 1126).  
Ch. B.

**Isoindole.** By W. STAEDEL and F. KLEINSCHMIDT (*Ber.*, 13, 836—837).—The best yield of bromoacetylbenzene,  $\text{Ph.CO.CH}_2\text{Br}$ , is obtained by allowing bromine to drop slowly into a solution of acetophenone (m. p.  $20.5^\circ$ , not  $16^\circ$  as generally stated) in carbon bisulphide. A rapid current of carbonic anhydride is passed through the solution, during the process, in order to carry off the hydrobromic acid which is liberated. When the reaction is completed, the carbon bisulphide is removed by evaporation, and after expelling the hydrobromic acid by

a stream of carbonic anhydride, the residue consists of crystals of pure bromacetylbenzene (m. p.  $50^{\circ}$ ). *Isoindole* is obtained in dark-red crystals by the action of alcoholic ammonia on the preceding compound at the ordinary temperature. A vapour-density determination at a temperature of  $500^{\circ}$  gave 6.5 instead of 4.05 for  $C_8H_7N$ .

W. C. W.

**Carbazol.** By C. GRAEBE (*Annalen*, 202, 19—23).—When crude anthracene is purified by distillation over potash (Perkin, *Journ. Soc. Arts*, 1879, 339), the residue consists chiefly of a compound of potassium and carbazol,  $(C_6H_4)_2NK$ , which is also obtained by heating carbazol and potash together at  $220$ – $240^{\circ}$ . Water decomposes it into potash and carbazol. Soda forms a similar compound; the action is, however, less complete.

P. P. B.

**Some Derivatives of Carbazol.** By C. GRAEBE and B. v. ADLERSKRON (*Annalen*, 202, 23—27).—*Methylcarbazol*,  $(C_6H_4)_2NMe$ , is prepared by heating carbazol, potash, and methyl iodide in sealed tubes at  $170$ – $190^{\circ}$ . It crystallises from hot alcohol in white lustrous leaflets; from dilute solutions, it separates out in needles (m. p.  $187^{\circ}$ ). It is insoluble in water, sparingly in cold, and easily soluble in hot alcohol. Ether dissolves it easily. It does not form salts, and with concentrated sulphuric and nitric acids, yields the same coloration as carbazol. With picric acid, it forms a compound,  $(C_6H_4)_2NMe + C_6H_2(NO_2)_3OH$ , crystallising in dark-red needles, easily soluble in alcohol, and melting at  $141^{\circ}$ .

*Ethylcarbazol*,  $(C_6H_4)_2NEt$ , is prepared in a manner similar to the methyl-derivative; it crystallises from ether, in which it is easily soluble, in leaflets (m. p.  $67$ – $68^{\circ}$ ); cold alcohol dissolves it sparingly, hot alcohol more easily: it is insoluble in water. Its picric acid compound forms light red needles (m. p.  $97^{\circ}$ ); easily soluble in alcohol.

*Ethylcarbazoline* is prepared by the action of ethyl iodide on carbazoline and alcohol at  $100^{\circ}$ ; it cannot be prepared from ethylcarbazol, since phosphorus and hydriodic acid by their action regenerate carbazol. Ethylcarbazoline iodide,  $C_{12}H_{14}N.EtHI$ , crystallises in large thick tables, easily soluble in hot water.

*Acetylcarbazoline*,  $C_{12}H_{14}N.Ac$ , formed by heating carbazoline with acetic anhydride at  $100$ – $120^{\circ}$ , crystallises from alcohol in beautiful white needles (m. p.  $98^{\circ}$ ). Alcohol and ether dissolve it easily. Ferric chloride and chromic acid attack it less easily than carbazol.

*Tetranitrocarbazol*,  $C_{12}H_8(NO_2)_4N$ , is prepared by adding carbazol to nitric acid and heating the mixture on the water-bath. It is insoluble in alcohol, ether, and benzene, but soluble in glacial acetic acid, from which it crystallises in yellow crystals. It forms a potassium compound which is insoluble in water, and is decomposed by acids.

P. P. B.

**Chloro-derivatives of Carbazol.** By W. KNECHT (*Annalen*, 202, 27—37).—*Trichlorocarbazol*,  $C_{12}H_5Cl_3N$ , is obtained by passing chlorine into a solution of carbazol in glacial acetic acid until it assumes a green colour, and then precipitating it with water. It crystallises from benzene in greenish needles (m. p.  $180^{\circ}$ ) easily soluble in benzene, ether, alcohol, and chloroform. It sublimes in needles, and

distils at a temperature near the boiling point of sulphur; by long-continued heating near its boiling point, it is decomposed with generation of carbazol. Hydrochloric acid dissolves it with a green colour, which is darkened on addition of nitric acid, and disappears when warmed. With picric acid it forms an unstable compound, crystallising in red needles (m. p. 100°).

**Hexachlorocarbazol**,  $C_{12}H_3Cl_6N$ .—By the continued action of chlorine on a solution of carbazol in glacial acetic acid, the solution becomes red, and the addition of water then precipitates this compound. It crystallises from benzene in long yellow needles, melting at 225° with decomposition. It is easily soluble in benzene, and less soluble in alcohol and glacial acetic acid. It can neither be sublimed nor distilled. Concentrated sulphuric acid dissolves it, forming a green-coloured solution in which traces of nitric acid produce a blue coloration, changing to violet, red, and finally yellow.

**Octochlorocarbazol**,  $C_{12}Cl_8NH$ , is formed by treating the hexachloro-derivative with antimony perchloride; it crystallises from benzene in beautiful white needles (m. p. 275°). It is easily soluble in hot benzene, and sparingly soluble in cold alcohol, ether, and glacial acetic acid. When suspended in sulphuric acid and treated with nitric acid, it yields a blue coloration, and finally a golden yellow.

The final product of the action of antimony perchloride on octochlorocarbazol is perchlorobenzene. P. P. B.

**Amidotriphenylmethane**. By O. FISCHER and L. ROSER (*Ber.*, 13, 674—676).—The previously unknown modification of amidotriphenylmethane is obtained by digesting benzhydrol with aniline hydrochloride and zinc chloride at 150°, thus:—



It crystallises from ether and light petroleum in prisms or plates (m. p. 84°), and forms a compound with benzene,  $C_{18}H_{17}N + C_6H_6$ ; this crystallises in colourless needles which melt partially at 69° with loss of benzene. The *platinochloride*,  $C_{18}H_{17}N.HCl)_2.PtCl_4$ , is a yellow crystalline precipitate, which is only sparingly soluble in hot water. The sulphate, chloride, and nitrate crystallise in pearly needles, which are scarcely soluble in water or alcohol. The *methiodide*,  $C_{22}H_{21}NI$ , obtained by heating the free base with methyl iodide and methyl alcohol at 100°, crystallises in colourless plates (m. p. 184°), and is identical with the compound obtained in a similar manner from dimethylamidotriphenylmethane. T. C.

**Diamidotriphenylmethane**. By O. FISCHER (*Ber.*, 13, 665—669).—In the author's first experiment (*ibid.*, 12, 1693) only a small quantity of this compound was obtained by the action of benzaldehyde on aniline hydrochloride, in presence of zinc chloride, the chief product being a resinous mass. This latter consists essentially of a compound of diamidotriphenylmethane with benzaldehyde, which, on boiling with dilute sulphuric acid, splits up into the above constituents; the aldehyde distils off, whilst the diamido-compound crys-



tallises out as the sulphate. An improved method, depending on this fact, is described for obtaining the base in larger quantities.

Diamidotriphenylmethane forms a colourless compound with benzene,  $C_{18}H_{18}N_2 + C_6H_6$  (m. p.  $106^\circ$ ), which, on heating to  $110^\circ$  or by the action of acids, splits up into benzene and the free base. The benzene compound is very soluble in light petroleum. The free base crystallises in colourless nodules (m. p.  $139^\circ$ ), which are easily soluble in ether, alcohol, chloroform, and light petroleum. The sulphate is only sparingly soluble in absolute alcohol, and crystallises from dilute alcohol in colourless needles. The *platinochloride*,  $C_{18}H_{18}N_2 \cdot 2HCl \cdot PtCl_4$ , is easily soluble in water and in alcohol, but only sparingly soluble in ether. The free base is converted into triphenylmethane when treated according to E. and O. Fischer's method (*Annalen*, 194, 270), and by the diazo-reaction it gives apparently dioxotriphenylmethane. On oxidation, it gives a colouring matter, which is bluer than methyl violet. The free base is identical with Böttlinger's diamidotriphenylmethane (*Ber.*, 11, 276, 840; *ibid.*, 12, 975; this Journal (1878), Abstr., 506, 723; (1879), Abstr., 716). His melting point ( $75^\circ$ ), however, was incorrect, owing to the presence of impurities.

T. C.

**A New Triamidotriphenylmethane (Pseudoleucaniline).** By O. FISCHER and J. ZIEGLER (*Ber.*, 13, 671—674).—Metanitrobenzaldehyde, when digested with aniline hydrochloride and zinc chloride at  $100^\circ$ , is converted into a new nitro-base, which is purified by means of its benzene compound,  $C_{18}H_{17}N_3O_2 + C_6H_6$ . The latter separates from solution in benzene in the form of lemon-yellow crystalline groups (m. p.  $81^\circ$ ). It is nearly insoluble in water, very easily soluble in ether and alcohol, less so in benzene, and only very sparingly soluble in light petroleum. The free nitro-base,  $C_{18}H_{17}N_3O_2$ , is obtained by heating its benzene derivative at  $110$ — $120^\circ$ . It consists of pale yellow crystals (m. p.  $136^\circ$ ), and on heating with an excess of methyl iodide and methyl alcohol at  $110$ — $115^\circ$ , it gives the compound  $C_{18}H_{22}N_3O_2 \cdot 2MeI$ , which crystallises from alcohol in needles (m. p.  $225^\circ$  with decomposition, the substance becoming green), and loses the whole of its methyl iodide at  $200^\circ$ . The residue appears to be converted into benzaldehyde green when oxidised with manganese dioxide and sulphuric acid (compare *Ber.*, 12, 802). The above methiodide is identical with the corresponding compound of meta-nitrotetramethyldiamidotriphenylmethane.

The nitro-base previously described gives triamidotriphenylmethane (pseudoleucaniline) when reduced with zinc-dust and hydrochloric acid. The benzene compound of pseudoleucaniline ( $C_{18}H_{18}N_3 + C_6H_6$ ) crystallises from benzene in white needles (m. p.  $145^\circ$ , with the previous evolution of gas). Pseudoleucaniline is obtained from its compound with benzene, by boiling with sulphuric acid until all the benzene has gone off, and then precipitating with ammonia. It crystallises from ether on addition of a little light petroleum, in brilliant colourless rosettes, which are very apt to retain ether. After drying at  $100^\circ$ , it melts at  $150^\circ$ . It is easily soluble in alcohol, less so in ether, and scarcely at all in light petroleum. It forms a methiodide, which appears to be a monomethylated triamidotriphenylmethane,

and cannot be obtained in the crystalline form. On heating at  $200^{\circ}$ , it loses its methyl iodide, and leaves a residue which, on oxidation, gives a dark green dye-stuff. The *platinochloride* of pseudoleucaniline,  $(C_{10}H_9N_3 \cdot 3HCl)_2 \cdot 3PtCl_4$ , is a yellow crystalline precipitate, which is very easily soluble in water, less soluble in alcohol, and still less so in ether.

Metanitrodiamidotriphenylmethane, on oxidation with hydrochloric acid at  $150^{\circ}$ , gives a fused mass, containing two dye-stuffs, which are easily separated by means of water. The more soluble is violet, and the other, which is obtained in larger quantity, is green. Pseudoleucaniline, under similar circumstances, gives only a violet dye-stuff, which is easily soluble in alcohol and in water. By this means pseudoleucaniline is readily distinguished from paraleucaniline.

T. C.

**Probable Occurrence of Furfurane (Tetraphenol) and a Homologous Compound in the Products of the Dry Distillation of Pine Wood.** By A. ATTERBERG (*Ber.*, 13, 879—883).—The low boiling portion of the wood oil obtained by the dry distillation of resinous pine wood, appears to contain tetraphenol; the fraction boiling at  $30^{\circ}$  seems to be a mixture of tetraphenol and valerylene, but neither of these bodies was obtained in a pure state.

*Sylvane*,  $C_4H_8O \cdot Me$  (b. p.  $63^{\circ}$ ), a homologue of tetraphenol, is contained in that portion of the distillate which passes over between  $59^{\circ}$  and  $65^{\circ}$ . It is a colourless liquid (sp. gr. 0.887), which is easily converted into a resinous tarry mass. On oxidation with potassium permanganate, it yields acetic acid. Hydrochloric acid converts sylvane into the compound  $C_{15}H_{22}O_2$  (b. p.  $235-245^{\circ}$ ).

W. C. W.

**Phenylnaphthylcarbazol.** By C. GRAEBE and W. KNECHT (*Annalen*, 202, 1—19).—In a former communication the authors have given some account of this body and some of its derivatives (*Ber.*, 12, 341), and also of its synthesis from  $\beta$ -phenylnaphthylamine (this vol., 168). Later determinations show its boiling point to be about  $450^{\circ}$ .

*Phenylnaphthylcarbazoline*,  $C_{18}H_{15}N$ .—This base is prepared by the action of phosphorus and hydriodic acid on phenylnaphthylcarbazol in sealed tubes at  $200^{\circ}$ . It is liberated from its salts by means of ammonia, and crystallises from alcohol in needles. It is easily soluble in alcohol and ether, and but sparingly soluble in water. Hydrochloric acid dissolves it, forming a salt, decomposed by boiling water. Platinum chloride produces an orange-yellow precipitate, which, on warming, turns red, and finally brown. On oxidation, phenylnaphthylcarbazoline yields phthalic acid.

*Phenylnaphthylcarbazoline iodide*,  $C_{18}H_{15}N \cdot HI$ , is prepared by dissolving the base in hydriodic acid. It crystallises in long colourless needles, which are soluble in water and alcohol, and sparingly soluble in ether. When oxidised by potassium dichromate and sulphuric acid, phenylnaphthylcarbazol yields phthalic acid and two quinones, viz.,  $C_{18}H_9O_2N$  and  $C_{18}H_9O_3$ ; these may be separated by means of sodium carbonate, which dissolves the latter. On adding an acid or by treatment with carbonic acid it may be reprecipitated.

**Phenylnaphthylcarbazquinone**,  $C_{16}H_8(O_2)N$ .—This body is purified by subliming the raw product, and crystallising it from glacial acetic acid; it sublimes in reddish-yellow needles, resembling alizarin, and melts at  $307^\circ$ . It is soluble in hot glacial acetic acid, in acetic ether and benzene, is sparingly soluble in alcohol, and insoluble in carbon bisulphide. It is insoluble in alkaline carbonates, but dissolves in caustic alkalis, forming a dark-red solution, from which acids reprecipitate it. These solutions, when treated with zinc-dust, turn brown, and finally yellow; the oxygen of the air produces the opposite effect. This quinone is oxidised to phthalic acid by potassium permanganate, and yields phenylnaphthylcarbazol when heated with zinc-dust.

**Quinone of phenylenenaphthalene oxide**,  $C_{16}H_8O:(O_2)$ .—This body crystallises from benzene in reddish-yellow prisms; it melts at a very high temperature, and is at the same time decomposed. It is soluble in hot glacial acetic acid and benzene, and sparingly soluble in alcohol. Alkalis and alkaline carbonates dissolve it, forming dark-red solutions, from which it is precipitated by carbonic acid in reddish-yellow flocks. When heated with zinc-dust, a compound is obtained which crystallises in yellow leaflets, melting at  $300^\circ$ , and having the composition  $C_{16}H_{10}O$ . To this compound the authors attribute the constitution

$\langle \begin{smallmatrix} C_6H_4 \\ C_{10}H_6 \end{smallmatrix} \rangle O$ , similar to that of diphenylene oxide. Unsuccessful attempts were made to prepare it by heating  $\beta$ -naphthol and phenol with lead oxide;  $\alpha$ -naphthol and phenol, however, yield a compound melting at  $150^\circ$ . To phenylnaphthylcarbazol and its quinone the authors attribute the formulæ  $\begin{smallmatrix} C_6H_4 \\ | \\ C_{10}H_6 \end{smallmatrix} \rangle NH$  and  $\begin{smallmatrix} C_6H_4 \\ | \\ C_{10}H_4(O_2) \end{smallmatrix} \rangle NH$ .

P. P. B.

**Synthesis of Naphthylidiphenylmethane.** By V. HEMILIAN (*Ber.*, 13, 678—679).—A claim to priority of discovery (*Jour. Russ. Chem. Soc.*, 12 [2], 4) of the above hydrocarbon over Lehne (*Ber.*, 13, 358; this vol., 478).

T. C.

**Colouring Matters attained by the Action of Naphthol on Diazoazobenzene.** By R. NIEZKI (*Ber.*, 13, 800—802).—The author claims the discovery of the colouring matter known as Biebrich scarlet, and denies the accuracy of the statements of W. v. Miller (this vol., 559) as to its composition. He will contribute a paper on the subject.

G. T. A.

**Rouge Français.** By W. v. MILLER (*Ber.*, 13, 268—271).—The dye sold under this name is a mixture of the sodium salts of two acids, naphthol-azobenzenesulphonic acid,  $SO_3H.C_6H_4.N_2.(S)C_{10}H_6.OH$ , and naphthol-azonaphthalenesulphonic acid,  $SO_3H.C_{10}H_4.N_2.(S)C_{10}H_6.OH$ . The first salt is yellow; the second red. The barium salts of both acids are sparingly soluble. The calcium salt of the yellow acid dissolves easily in hot water; that of the red with difficulty. The commercial product is probably formed by acting with  $\beta$ -naphthol on a diazotized mixture of sulphanilic and naphthylaminesulphonic acids. A mixture of 30 parts of yellow salt with 70 parts red dyes the same shade as rouge français.

Ch. B.

**Fluorescence in the Anthracene Series.** By C. LIEBERMANN (*Ber.*, 13, 913—916).—An examination of solutions of the anthracene derivatives in indifferent solvents shows that the property of fluorescence is exhibited by those substances in which the two benzene nuclei are united by a group having the constitution  $\langle \begin{smallmatrix} \text{CM} \\ \text{CM} \end{smallmatrix} \rangle$  (where M represents a monad element or group of elements), but not by those derivatives containing the double ketone group  $\langle \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \rangle$  or the group  $\text{Ph.C(OH):CO}$ . W. C. W.

**Derivatives of the Quinone from the Hydrocarbon  $\text{C}_{18}\text{H}_{12}$ ; Polymeric Quinones.** By A. BREUER and T. ZINKE (*Ber.*, 13, 631—635).—In a previous communication (*ibid.*, 11, 1995; this Journal, 36, 327), it has been shown that the quinone  $\text{C}_{18}\text{H}_{10}\text{O}_2$  gives a hydroxyimidoquinone  $\text{C}_{18}\text{H}_9(\text{OH}):(\text{O.NH})$  when treated with ammonia. Corresponding derivatives have since been obtained by using various amines in place of ammonia.

*Methylamine derivative*,  $\text{C}_{18}\text{H}_9(\text{OH}):(\text{O.NMe})$  consists of dark red leaflets (m. p.  $170^\circ$ ), which are but sparingly soluble in cold alcohol, more easily in hot, and easily soluble in benzene. It dissolves in concentrated sulphuric or hydrochloric acid with a dark red colour, and is precipitated therefrom on addition of water. It gives the hydroxyquinone and methylamine, when heated with fuming hydrochloric acid at  $140$ — $150^\circ$ . It is slowly attacked by aqueous, but more easily by alcoholic potash, with formation of the hydroxyquinone.

*Ethylamine derivative*,  $\text{C}_{18}\text{H}_9(\text{OH})\text{SO}:(\text{O.NEt})$  forms dark brown needles (m. p.  $130^\circ$ ), which are soluble in concentrated sulphuric acid, without change.

*Aniline derivative*,  $\text{C}_{18}\text{H}_9(\text{OH}):(\text{ON.Ph})$ , consists of dark red leaflets (m. p.  $158^\circ$ , which are only sparingly soluble in alcohol, but more easily in benzene. It dissolves unchanged in concentrated sulphuric acid, with a deep violet colour. Fuming hydrochloric acid at  $150^\circ$  converts it into the hydroxyquinone and aniline.

*Toluidine derivatives*,  $\text{C}_{18}\text{H}_9(\text{OH}):(\text{O.NC}_6\text{H}_7)$ .—The ortho-derivative is a red body, crystallising in needles (m. p.  $108^\circ$ ), and the para-compound, a brownish-violet body, also crystallising in needles (m. p.  $155^\circ$ ). The ortho-compound dissolves in strong sulphuric acid with a red, and the para-compound with a violet colour.

*Naphthylamine derivative*,  $\text{C}_{18}\text{H}_9(\text{OH}):(\text{O.NC}_{10}\text{H}_7)$ , crystallises in brownish-red needles (m. p.  $148^\circ$ ) which dissolve in strong sulphuric acid, with a violet colour. Trimethylamine, formamide, and acetamide have no action on the quinone, whilst dimethylamine forms only resinous products. All the above compounds, when treated with reducing agents, give colourless products, the nature of which varies with the reducing agents employed. Zinc and hydrochloric acid, as well as zinc-dust and an alkali, give compounds which could not be isolated, but on exposure to air are reconverted into the original coloured substances. They are all easily reduced by ammonium sulphide, which, when added in excess, throws down the reduction product. The aniline derivative under these circumstances gives colourless crystals (m. p.

290°). Reduction with aqueous sulphurous acid gives the hydroxyquinone, together with a black compound, the nature of which has not yet been fully investigated. This body crystallises from benzene or light petroleum in dark steel-blue needles (m. p. 186°), which dissolve in alcohol with a yellow colour, and is reprecipitated therefrom unchanged on addition of water. Long treatment with alcohol, however, converts it into hydroxyquinone. It does not contain nitrogen, and analysis gave 78.76 per cent. C., and 4.88 per cent. H. It is probably an anhydride of the hydroxyquinone  $[C_{15}H_{19}(OH)_2]_2O$ .

The authors have shown (*Ber.*, 11, 1403; this *Journal*, 1878; *Abstr.*, 889) that solutions of the quinone  $C_{16}H_{10}O_2$ , exposed to sunlight, give two sparingly soluble compounds. These were found to be polymeric modifications; they are separated by treatment with chloroform, in which one is more soluble than the other.

The *more soluble modification* crystallises in small yellow rhombic tables (m. p. 225—229°) which are but little soluble in most solvents; they dissolve most easily in chloroform, and in hot glacial acetic acid. It is not easily reconverted into the ordinary form by heat. It is not attacked by chromic mixture, and only slowly by a mixture of chromic and glacial acetic acids, giving thereby benzoic acid; by potassium permanganate, it is oxidised to benzoic and phthalic acids. By the action of alcoholic potash, it gives an almost black compound, which, on exposure to the air and washing with alcohol, becomes yellow, the same change being more quickly produced by water or by warming with alcohol. This compound crystallises from glacial acetic acid in fine yellow needles (m. p. above 300°), which are but little soluble in alcohol, benzene, or chloroform. Analysis gave the numbers 79.23 per cent. C., and 4.65 per cent. H., and it has therefore the same composition as the reduction product from the amine derivatives of the quinone (*vide supra*), and is probably a polymeric modification of the same. It dissolves in alcoholic but not in aqueous potash; it dissolves in strong sulphuric acid, with a brownish-green colour, whilst its solution in strong nitric acid is almost colourless; water precipitates it unchanged from both solvents. It is apparently converted into an acetyl derivative by treatment with acetic chloride or anhydride, showing that it probably contains hydroxyl groups.

The *less soluble polymeric modification of the quinone* consists of white leaflets (m. p. 207°), which on heating are easily converted into the ordinary quinone. It is not attacked either by potassium permanganate or by chromic mixture; on oxidation with chromic and glacial acetic acids, however, it gives benzoic acid. It acts in an entirely different manner to the more soluble modification, when treated with alcoholic potash. The reaction, which is very complicated, appears to give rise to a polymeric hydroxyquinone.

T. C.

**Chemistry of Bast Fibres.\*** By E. J. BEVAN and C. F. CROSS. —The authors' investigations have been confined to jute and esparto, the former as a peculiarly typical bast fibre, the latter as representing monocotyledonous growth.

\* A Paper read before the Owens College Chemical Society, 16th April. Published by Palmer and Howe, Manchester. See also *Chem. News*, 42, 77.

The *inorganic* constituents of the normal jute fibre are—

(a.) *Water of hydration*, varying from 10 to 12 per cent. of its weight, with the temperature and hygrometric state of the air. It is to be regarded as dependent both on the chemical nature and structure of the fibre (chemical adhesion), although scarcely upon its external structure (capillarity), as conjectured by Sir W. Thompson.

(b.) *Ash*.—The general features of the inorganic skeleton of this fibre may be expressed by the following average percentage numbers:— $\text{SiO}_2$ , 30–35;  $\text{Fe}_2\text{O}_3$ , 5–8;  $\text{Al}_2\text{O}_3$ , 5–6;  $\text{Mn}_2\text{O}_3$ , 0.5–0.9;  $\text{CaO}$ , 13–16;  $\text{K}_2\text{O} + \text{Na}_2\text{O}$ , 5–10;  $\text{P}_2\text{O}_5$ , 8–13;  $\text{SO}_3$ , 1–5.

(c.) *Organic* (considered with exclusion of *a* and *b*). Combustions of the fibre (purified by boiling in dilute ammonia; the fibre thereby sustains a loss of 1 per cent. of its weight, losing a resinous constituent, which causes the adhesion of portions of cortical parenchyma, and the matting together of the fibres in the raw state), showed it to have the following aggregate (average) composition: C, 46.5; H, 5.80. Nitrogen is present only in minute quantity, e.g., in a fair specimen (previously boiled in dilute sodium carbonate) the quantity determined was 0.053 per cent. The proximate constituents of the fibre are, *cellulose*, 70 per cent., as isolated by the ordinary methods, and *inter-cellular and encrusting substance*, 30 per cent.

Hugo Müller's method for the quantitative determination of cellulose gives satisfactory results with this fibre; identical results are obtained, but in a very much shorter time, by substituting *chlorine* gas for the bromine-water, the fibre being boiled previously to chlorination in a weak alkaline solution. The action of the gas is to form a definite compound with the aromatic portion of the fibre, which is decomposed on boiling with ammonia, with formation of soluble products. Pure cellulose is obtained on once repeating this treatment, whilst if bromine-water is used, several repetitions (5–6) are necessary. A modification of this method, involving points discussed in another connection, consists in boiling the chlorinated fibre with a solution of sodium sulphite (5 per cent.) for a few minutes, and subsequently with an alkali (a solution of potash, 1 per cent., is a better solvent for the products of decomposition, and its use does not affect the yield of cellulose); by the method thus modified pure cellulose is at once obtained. It is a remarkable fact that the yield of cellulose is, in this case, 5 per cent. higher than by either of the two previous methods. There is additional evidence to show that jute cellulose is a chemical aggregate, and therefore to a certain extent defined by the process by which it is obtained. The above-mentioned chlorine derivative is a definite compound,  $\text{C}_{18}\text{H}_{18}\text{Cl}_4\text{O}_9$ ; it has been obtained and purified in different ways, but with constant analytical results. It is soluble in alcohol and glacial acetic acid, and is precipitated from its solution on the addition of water, in yellow flocks; it dries to an amorphous yellowish powder, which has an odour closely resembling that of tetrachloroquinone. It further resembles this compound in dissolving in ammonia to a purple solution, changing to brown on standing. The analogies of this body to the quinone derivatives are unmistakable; the authors are therefore able to confirm Hugo Müller's observation of the presence of a body having the reaction of a quinone in the inter-

cellular substance of bast fibres. The most striking reaction of this derivative is the development of a pure magenta purple colour, of great brilliancy when treated with a solution of sodium sulphite. This is best seen in the freshly chlorinated fibre; all bast fibres examined by the authors (flax, hemp, manilla, &c.) gave the same coloration after chlorination. Upon the reactions of these bodies the method for the isolation of cellulose proposed by the authors was based, the chlorine body being converted by the sodium sulphite into soluble (reduction) products. Being a recent observation it is still under investigation.

A similar derivative was obtained from esparto. The brown solution obtained by heating the substance under pressure with an alkaline lye, yields a flocculent precipitate when neutralised. After purification by twice dissolving in glacial acetic acid, and reprecipitating by water, it has the aggregate composition  $C_{31}H_{24}O_8$  (it contains also 1.2 per cent. nitrogen). This body on heating with hydrochloric acid and potassium chlorate, yields the chlorine derivative,  $C_{23}H_{23}Cl_4O_{10}$ , which is also to be regarded as formed from a complicated quinone.

The quinone of the jute fibre appears to be associated with a carbohydrate. By the action of dilute sulphuric acid (5 per cent.) at  $80^\circ$ , a soluble carbohydrate is formed, and is obtained after purification as a brown, sticky, hygroscopic solid, having the composition  $C_{14}H_{18}O_9$ . As no other products are formed, the aromatic portion of the fibre resisting the action of the acid, and the loss of weight (23 per cent. in a certain case) falling to a large extent on the intercellular substance, this, it must be inferred, contains a carbohydrate. The same conclusion is arrived at by a study of the action of alkalis on the fibre, and of a peculiar fermentation, which is induced under certain conditions of moisture and high temperature, by which this portion undergoes resolution. The carbohydrate associated with the quinone is rather of the nature of cellulose than glucose; the fact that by a certain decomposition of the intercellular substance the yield of cellulose is increased, goes to show that a portion of the "aggregate" cellulose obtained is a product of such decomposition. The authors therefore regard the intercellular substance of this bast fibre as a "cellulide," or more specifically a cellulosequinone. Upon this constituent depends the integrity and remarkable dyeing capacity of the fibre; *pari passu* with its removal, these disappear, until in the isolated cellulose there is obtained a mass of disintegrated cells, having no affinity for colouring matters.

By the action of nitric acid (5 per cent.) this cellulosequinone is entirely converted into soluble products. The aromatic portion of these are more conveniently studied in the analogous esparto derivative. From the solution obtained by digesting the acid on the resinous precipitate before described, a peculiar nitro-derivative was obtained. Concordant analyses of this body, in the form both of its barium and calcium compound, established the formula as



In the free state it is a powerful acid; it has an intensely bitter taste, and dyes animal fibres a brilliant yellow.

C. F. C.

**Hydrocamphene.** By J. KACHLER and F. V. SPITZER (*Ber.*, 13, 615—616).—The authors have previously shown (*Annalen*, 200, 340) that the unsaturated hydrocarbon camphene,  $C_{10}H_{16}$ , may be considered as the nucleus of all the compounds of the camphor group. *Hydrocamphene*,  $C_{10}H_{18}$ , is obtained, together with camphene, by acting on a benzene solution of borneol chloride,  $C_{10}H_{17}Cl$  (or of camphor dichloride,  $C_{10}H_{16}Cl_2$ ) with sodium. The mixture of the two hydrocarbons, after saturation with hydrochloric acid (so as to convert the regenerated camphene into the chloride), is again treated with sodium, and this operation repeated ten times. The product, which solidifies to a crystalline mass, is finally purified by sublimation, when the hydrocarbon is obtained as a hard brittle mass (m. p.  $140^{\circ}$ ) resembling stearic acid. It is easily soluble in ether, but less soluble in alcohol and acetic acid, and sublimes even at the ordinary temperature. Hydrocamphene is possibly identical with the hydrocarbon  $C_{10}H_{18}$ , obtained by Montgolfier (*Chem. Centr.*, 1879, 52), by the action of sodium on the fused hydrochloride of turpentine oil. T. C.

**Action of Sodium on Turpentine Hydrochloride.** By E. A. LETTS (*Ber.*, 13, 793—796).—When turpentine hydrochloride is fused with sodium, and the product distilled after removal of the chlorine, a fine white solid (m. p.  $157^{\circ}$ ) is obtained as the chief product, but on raising the temperature, a yellowish-white liquid (b. p.  $326$ — $330^{\circ}$ ) passes over, which solidifies in feathery crystals, resembling sal-ammoniac.

The first of these bodies melts at  $94^{\circ}$ , and is supposed by the author to have the composition  $C_{10}H_{17}$ , and not that of a mixture of  $C_{10}H_{16}$  and  $C_{10}H_{18}$ . The second body also melts at  $94^{\circ}$ , and consists of  $C_{20}H_{34}$ . It is extraordinarily stable. The mother-liquor remaining after the crystallisation of this body has the same boiling point and composition as the crystals, so that there seem to be two modifications of a new hydrocarbon,  $C_{20}H_{34}$ .

The so-called liquid turpentine hydrochloride, when acted on by sodium, yields a solid, which is identical with the second solid body obtained above.

Montgolfier, who has repeated the author's experiments (*Compt. rend.*, 87, 840—842) finds that the first described solid, with lower boiling point, is a mixture of inactive camphene,  $C_{10}H_{16}$ , and camphene hydride,  $C_{10}H_{18}$ , and has isolated the two bodies from the mixture. He gives the melting point of camphene hydride as  $120^{\circ}$ . He has also obtained the liquid hydrocarbon with higher boiling point, and names it colophene hydride,  $C_{20}H_{34}$ .

By the action of sodium on liquid turpentine hydrochloride, he has obtained two liquids,  $C_{10}H_{18}$ , boiling at  $165$ — $166^{\circ}$ , and  $C_{10}H_{16}$ , boiling at  $178^{\circ}$ . He has also isolated small quantities of the solid  $C_{10}H_{18}$  from the product of the last reaction (compare Kachler and Spitzer, preceding abstract). G. T. A.

**Action of Ammonia on Ethyl Camphoronates.** By E. HJELT (*Ber.*, 13, 796—799).—There are two isomeric monethyl camphoronates, one of which is a liquid, and the other a solid, consisting of



colourless tabular crystals (m. p.  $67^{\circ}$ ). When acted on by dry ammonia gas, the former yields a monamide (m. p.  $212^{\circ}$ ),  $C_9H_{13}NO_4$ , the latter an amido-amide (m. p.  $144-145^{\circ}$ ),  $C_9H_{13}N_2O_4$ . An amido-acid could not be obtained from the amido-amide.

Ammonia acts also on diethyl camphoronate when the two are heated in sealed tubes at  $115-130^{\circ}$ , with formation of an amido-amide (m. p.  $160^{\circ}$ ),  $C_9H_{13}N_2O_4$ , which yields an acid,  $C_9H_{13}NO_5$  (m. p.  $212^{\circ}$ ), but this does not exhibit the ordinary reactions of an amido-acid. The author supposes that the formation of amido-amines instead of diamines arises from the hydroxyl group being placed between two carbon atoms, which are united with oxygen.

G. T. A.

**Ethereal Oil from the Californian Bay Tree.** By J. M. STILLMAN (*Ber.*, 13, 629-631).—The leaves of the Californian bay tree (*Onodaphne Californica*) when distilled with steam yield nearly 3 per cent. of a clear, limpid, yellow oil, having a pleasant aromatic odour, but producing tears when strongly inhaled; sp. gr.  $0.94$  at  $11^{\circ}$ . By fractional distillation, it may be separated into terpinol ( $C_{10}H_{17}O$ ), b. p.  $167-168$ , and Umbellol,  $C_8H_{12}O$ , b. p.  $215-216^{\circ}$ . V. d. =  $4.39$ , calc. =  $4.29$ .

Umbellol is a colourless limpid liquid, having a pleasant odour, but producing tears and headache when inhaled in larger quantity. It is insoluble in water, and but slightly volatile therewith. It dissolves in concentrated sulphuric acid with a blood-red colour, which rapidly becomes black. It is strongly attacked by sodium or by concentrated nitric acid.

T. C.

**Abietic Acid.** By W. KILBE (*Ber.*, 13, 888-891).—Abietic acid,  $C_{20}H_{30}O_2$ , is obtained by adding common salt to the solution of soda which has been used for the purpose of purifying crude rosin oil. The soap is dried at  $70-80^{\circ}$ , and extracted with ether to remove impurities; the residue dissolves in alcohol, and on evaporation the alcoholic solution deposits needle-shaped crystals of sodium abietate. On the addition of hydrochloric acid to the aqueous solution of the sodium salt, a white precipitate of abietic acid is produced, which melts to a resinous mass if the mixture is boiled. The acid is soluble in ether, benzene, alcohol, and glacial acetic acid, and is deposited from its solution in the latter solvent in triclinic plates (m. p.  $165^{\circ}$ ). The pure salts of abietic acid form gelatinous masses with ether, but do not dissolve in it.

W. C. W.

**Caryophyllin.** By E. HJELT (*Ber.*, 13, 800).—Caryophyllin has the same empirical formula as camphor, but Mylius (*Ber.*, 6, 1053) prefers to double its formula. On oxidation with concentrated nitric acid it yields caryophyllic acid,  $C_{20}H_{32}O_6$ . Heated with acetic acid at  $100^{\circ}$ , it gives rise to an acetyl-derivative, which crystallises in the monoclinic system, and melts at  $184^{\circ}$ . Two chlorine compounds are formed by the action of phosphorus pentachloride,  $C_{40}H_{64}O_2Cl$  and  $C_{20}H_{32}O_2Cl_2$ . The author concludes that the formula of caryophyllin is  $C_{20}H_{32}O_4$ . Cymene has not yet been obtained from it.

G. T. A.

**Caroba Leaves.** By O. HESSE (*Annalen*, 202, 150—151).—These leaves, which were formerly (*Ber.*, 10, 2164) supposed to be derived from the tree yielding the Pereiro bark, belong to a Brazilian tree, viz., *Cybistas antisyphilitica* (Marlino), or *Jacaranda procera* (Sprengel). Extracts from these, e.g., Rey's Brazilian injection, are supposed to have great efficacy in cases of syphilis. An investigation of these extracts has shown that no alkaloids are present.

P. P. B.

**Glycyrrhizin.** By J. HABERMANN (*Chem. Centr.*, 1880, 253—256, 267—271, 282—287).—The present paper gives in detail an account of the author's further investigations on glycyrrhizin and its decomposition products. He shows—(1.) That glycyrrhizic acid on boiling with dilute sulphuric acid decomposes into parasaccharic acid and glycyrrhetin. Sugar was not found among the decomposition products. (2.) That parasaccharic acid is distinguished from ordinary saccharic acid by affording no crystallisable salt. (3.) That pure glycyrrhetin is a crystalline, almost indifferent nitrogenous body, which gives very characteristic products with bromine, nitric acid, and acetic chloride, but does not yield paroxybenzoic acid on being fused with potash. (4.) That commercial ammoniacal glycyrrhizin, besides containing glycyrrhizic acid, also contains (a) amorphous glycyrrhizin bitter, and a nitrogenous compound of an intensely bitter taste. It occurs in subordinate quantities only. (b.) Dark brown glycyrrhizin resin, soluble in alcohol and in alkaline aqueous solutions to yellow-coloured liquids, also fusible with caustic potash, and yielding along with a resinous compound various volatile fatty acids and paroxybenzoic acid.

J. T.

**Hypochlorin and its Origin.** By PRINGSHEIM (*Chem. Centr.*, 1880, 299—304, 316—319, 331—334).—In an earlier paper (*ibid.*, 9 and 27), the author has made known the existence of hypochlorin. By the action of dilute hydrochloric acid on chlorophyll globules, semi-fluid masses of irregular form, reddish or brownish in colour, make their appearance, and out of these obscurely crystalline forms separate. These appearances show the presence of hypochlorin, and afford an unfailing reaction for this new body. The properties of the new body are difficult to investigate. The separated masses seem to consist of an oily mother-substance, which bears a closer analogy to ethereal oils than to fatty ones. The masses are insoluble in water, in salt solutions, in dilute mineral and organic acids, but are easily soluble in ether, benzene, carbon bisulphide, and ethereal oils, and also with more or less difficulty in alcohol, even when considerably diluted. The constituents of hypochlorin have not yet been ascertained. By hypochlorin the author means the crystalline forms above named. The hypochlorin reaction may be obtained without hydrochloric acid. Green textures preserved in glycerol or in calcium chloride solution show it here and there after a time. Treatment with warm or hot water in some cases, and with steam, forms one of the easiest means of separation.

In sprouting angiosperms no trace of hypochlorin can be detected until the plant has been exposed to light, and exposed longer than is

required to turn the plant green, whilst in gymnosperms which are peculiar as forming chlorophyll colouring matters in the dark, hypochlorin is also formed in plants grown in the dark. J. T.

**Synthesis of Quinoline.** By W. KOENIGS (*Ber.*, 13, 911—913).—Quinoline is formed by the dry distillation of acroleinaniline, and may be purified by Baeyer's method (*Ber.*, 12, 460), viz., by treatment with potassium chromate and sulphuric acid. The best method for preparing quinoline is by acting on a mixture of nitrobenzene, aniline, and glycerol with sulphuric acid. In this process it is probable that acroleinaniline is formed as an intermediate product.

W. C. W.

**Nicotine Derivatives.** By A. CAHOURS and A. ETARD (*Compt. rend.*, 90, 275—280).—When thiotetrapyridine,  $C_{10}H_{10}N_4S$ , obtained by the action of sulphur on nicotine (*ibid.*, 88, 999, and this Journal, 36, 732), is boiled with dilute nitric acid, it gives nicotinic acid (m. p. 228—229°).

Thiotetrapyridine when distilled with finely divided metallic copper loses sulphur, and yields a base, *isodipyridine*,  $C_{10}H_{10}N_4$ , isomeric with dipyridene, but differing greatly from it in its properties. It is also produced in small quantity by the action of alcoholic potash on thiotetrapyridine at 200°. Isodipyridene is a colourless oil (b. p. 274—275°), having an odour somewhat resembling that of certain mushrooms. It does not solidify at  $-20^\circ$ , and its sp. gr. at  $13^\circ$  is 1.1245. It is insoluble in cold, and only sparingly soluble in boiling water, but easily in alcohol or ether. It unites energetically with hydrochloric acid, but the hydrochloride does not crystallise. The *platinochloride*,  $(C_{10}H_{10}N_4.HCl).PtCl_4 + 2H_2O$ , crystallises in deep orange plates of the colour of potassium dichromate. It is decomposed if boiled with water.

It was thought probable that if nicotine were submitted to limited oxidation it might yield isodipyridine, thus:  $C_{10}H_{14}N_2 + O_2 = C_{10}H_{10}N_4 + 2H_2O$ . For this purpose pure nicotine was dissolved in dilute potash solution, and oxidised with potassium ferricyanide, and the product distilled. The bases extracted from the distillate by means of ether, when submitted to fractional distillation, were found to consist of isodipyridine mixed with unaltered nicotine.

If nicotine in the state of vapour is passed over red-hot porcelain, it is in part decomposed (about 20 per cent.), yielding a gaseous mixture of hydrogen with paraffins and olefines, and a liquid product containing pyridine, picoline, collidine, and new basic substances boiling at temperatures above  $250^\circ$ .

C. E. G.

**Formation of Hypoxanthine from Albuminoids.** By E. DRECHSEL (*Ber.*, 13, 240—242).—Salomon, Krause, and Chittenden are of opinion that the hypoxanthine observed in the solutions obtained from certain albuminoids by digestion, incipient putrefaction, or the action of dilute acids, does not exist as such in the albuminoids, but is a decomposition product. Thus Salomon could not detect it by ammoniacal silver nitrate in the aqueous extract, hot or cold, from well washed fibrin; and Chittenden did not observe it in the alcoholic extract, unless the

alcohol had been boiled with the fibrin for twelve hours. The author does not regard these experiments as conclusive, for fibrin as usually prepared must necessarily include other blood constituents, which could only be removed with great difficulty; and, on the other hand, Salkowski has shown (*Pflüger's Archiv.*, 4, 94) that the precipitation of hypoxanthine by ammoniacal silver nitrate does not take place in mixtures containing gelatin. The author has been unable by this reagent to detect purposely added hypoxanthine in the liquid obtained by heating fibrin with water in a digester. Again, there is no proof that the small quantity of hypoxanthine detected by Chittenden in the acid liquid obtained on boiling eggs with dilute acetic acid, and considered by him to exist as such in the egg, was not formed from the albumin during coagulation. The origin of hypoxanthine is therefore still uncertain. Ch. B.

**Morphine Hydrochloride.** By O. HESSE (*Annalen*, 202, 151—152).—By dissolving this body in methyl alcohol, and allowing it to stand, crystalline grains separate, which increase in quantity after some time, the quantity being also increased by warming. These crystals are anhydrous morphine hydrochloride,  $C_{17}H_{19}NO_3 \cdot HCl$ . It is sparingly soluble in ethyl or methyl alcohols, from which it separates as a shining crystalline powder, or in short four-sided rhombic prisms. One part of it dissolves in 51 parts of methyl alcohol. From water it crystallises in the ordinary hydrated form, which by solution in absolute alcohol is partially converted into the anhydrous form.

P. P. B.

**Action of Phosphorus Pentachloride and Oxychloride on Cinchonine Hydrochloride.** By W. KOENIGS (*Ber.*, 13, 285—287).—The mode of union of the oxygen in cinchonine and quinine is still unknown. According to Wright the acetyl and benzoyl derivatives described by Schützenberger are really derived from the isomeric bases cinchonidine and quinidine. Zorn (*J. pr. Chem.*, 8, 279), by the action of fuming hydrochloric acid at  $140-150^\circ$ , obtained the chlorinated bases  $C_{20}H_{23}N_2Cl + H_2O$  and  $C_{20}H_{23}N_2OCl + H_2O$  from cinchonine and quinine respectively. These retain chlorine and water with great obstinacy, and cannot be reconverted into the alkalis. Zorn regards them as formed by displacement of hydroxyl by chlorine, whilst Hesse (*Annalen*, 174, 340), looks on them as addition compounds. By a similar process, Skraup (*Ber.*, 12, 1107) obtained from cinchonine a brominated base,  $C_{19}H_{23}N_2OBr + H_2O$ , which parts with its bromine when heated with silver oxide, forming a very soluble and unstable base. Since cinchonine yields formic acid by oxidation with permanganate, Skraup supposes that it contains the group  $OCH_3$ , and that the nascent methyl bromide formed from this combines with the nitrogen to form the bromide of an ammonium base. Finally, Wischnegradsky (*Ber.*, 12, 1480) regards cinchonine as a ketone, its reduction products,  $(C_{19}H_{23}N_2O)_2H_2$  and  $C_{19}H_{23}N_2O$ , being related to it as pinacone and isopropyl alcohol are to acetone.

Neither phosphoric chloride nor oxychloride acts on cinchonine; but when 6—7 parts of oxychloride are gradually added to 1 part of cinchonine hydrochloride (dried at  $110^\circ$ ) mixed with 2 parts of phos-

phoric chloride, the mass becomes warm, and hydrochloric acid is evolved: the reaction having been completed by prolonged heating at 80—100°, the cooled product is poured into ice-cold water. On adding ammonia to this solution, a resinous precipitate first falls, and on continuing the addition a white crystalline mass slowly separates. When crystallised from dilute alcohol, this forms broad needles (m. p. 52°), soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide, sparingly so in boiling water. The results of analysis agree best with the formula  $C_{13}H_{21}N_2Cl$ . The body is probably, therefore, cinchonine, in which hydroxyl has been replaced by chlorine. Its hydrochloric acid solution gives a crystalline precipitate with platinic chloride. Hot alcoholic potash or sodium amalgam at ordinary temperatures remove chlorine from it, by which reaction it is distinguished from Zorn's chlorocinchonide,  $C_{20}H_{25}N_2OCl$ , which is not so affected. Ch. B.

**Hyoscyamine.** By A. LADENBURG (*Ber.*, 13, 254—256).—When hyostyamine is digested at 60° with baryta-water, it is decomposed; on precipitating the baryta with carbonic anhydride, acidifying with hydrochloric acid, and shaking with ether, *hyoscinic acid* (m. p. 116—117°) is obtained. This acid is probably identical with tropic acid from atropine (m. p. 117—118°), which it resembles in physical properties. Like that acid, when heated with dilute potassium permanganate solution, it gives an odour of bitter almond oil, and yields benzoic acid on treatment with excess of the oxidant. Moreover, when boiled for seven hours with twice its weight of barium hydrate, it is converted into atropic acid,  $C_8H_8O_3$ .

After removal of the hyoscinic acid and addition of potash, ether extracts from the residue a base, *hyoscine*, having approximately the composition  $C_8H_{13}NO \cdot \frac{1}{2}H_2O$ , which is that of a hydrated tropine (Kraut, *Annalen*, 133). Dry tropine melts at 61·5 (Kraut); but the author has frequently observed a melting point of 50° for it. Hyoscine prepared as above melts at 47—50°, b. p. 229°.

Its platinochloride has the composition  $(C_8H_{13}NOHCl)_2 \cdot PtCl_4$ . The formula  $C_8H_{13}N$ , assigned to it by Höhn and Reichardt, is therefore incorrect. This salt, as well as the picrate and aurochloride, cannot be distinguished from the corresponding salts of tropine.

Hyoscyamine and atropine are undoubtedly different, but wherein the difference lies has yet to be discovered. Ch. B.

**Hyoscyamine and Atropine.** By A. LADENBURG (*Ber.*, 13, 607—609).—The author has in a previous communication (see above) directed attention to the great similarity between hyoscinic and tropic acids. Subsequent measurements of the crystals of the platinochlorides of hyoscine and tropine show that they are identical. Hyoscine,  $C_8H_{13}NO$ , prepared from daturine, which the author has shown to be identical with hyoscyamine, crystallises from toluene in large clear crystals (m. p. 62°, b. p. 229°), which are so exceedingly hygroscopic that even after but slight exposure to the air the melting point sinks to 50°, which explains the earlier melting point found for this sub-

stance. On a strict comparison of hyoscyne and tropine from atropine no difference could be detected between them.

Hyoscinic acid and hyoscyne respectively were treated with dilute hydrochloric acid on a water-bath, the alkaloid so obtained precipitated with potassium carbonate, dissolved in chloroform, and evaporated; the residue was then dissolved in dilute hydrochloric acid and precipitated with gold chloride, when an aurochloride was obtained identical in every respect with that from atropine. By this means hyoscyamine is converted into atropine, and all doubt as to the identity of their decomposition products is removed. Atropine and hyoscyamine are most probably physical isomerides. T. C.

**Duboisine.** By A. LADENBERG (*Ber.*, 13, 257—258).—In composition and in analytical and physical characters, this alkaloid, obtained from the Australian plant *Duboisia myoporoides*, is identical with hyoscyamine. Ch. B.

**Tropidine.** By A. LADENBERG (*Ber.*, 13, 252—254).—Besides the ways already mentioned (*Ber.*, 12, 944), tropidine may also be formed by heating tropine at 220° with an equal weight of sulphuric acid, diluted with twice its volume of water. The greater part of the tropine is thus converted into tropidine, the remainder being decomposed in a more complex way. The tropidine may be separated by distillation with potash, and extracted from the distillate by ether. The aqueous solution of the base so prepared is not rendered turbid by a further addition of water, and its solution in hydrochloric acid does not become coloured on evaporation. These appearances, formerly described as characteristic, were due to impurities.

The aurochloride and platinochloride of the base were analysed. The latter ( $C_8H_{13}N.HCl$ ),  $PtCl_4$ , is dimorphous, crystallising in the monoclinic and rhombic systems. Its crystallographic constants have been accurately determined. Ch. B.

**Pereiro Bark.** By O. HESSE (*Annalen*, 202, 141—149).—An extract from this bark is used in Brazil as a febrifuge. The bark is obtained, according to Peckolt, from *Geissospermum velosii*, whilst according to Baillon, it is from *Geissospermum laeve*. Graps (*Repert. Pharm.*, 76, 32) finds it to contain an alkaloid, which is styled pereirine; whilst Peretti (*Jour. Chim. Med.*, 26, 162) concludes that it contains other alkaloids. The author has obtained from this bark two alkaloids, viz., geissospermine and pereirine. The alcoholic extract of the bark is treated with soda, and then extracted with ether. The ethereal extract is subsequently treated with acetic acid, and the dark-brown acetic acid solution is shaken up with ammonia and ether. Geissospermine then separates out, and the pereirine remains dissolved in the ether, and is obtained by evaporating the ethereal solution.

*Geissospermine*,  $C_{19}H_{24}N_2O_2 + H_2O$ , crystallises from alcohol in small white prisms, the ends of which are surmounted by domes. It dissolves easily in hot, and sparingly in cold alcohol, the solution having an alkaline reaction. It is insoluble in ether and water. It dissolves easily in dilute acids, and is precipitated from these solutions by

alkalis. Concentrated nitric acid gives a purple-red coloration, which when heated, becomes orange-yellow. Its solution in pure concentrated sulphuric acid is at first colourless; it however becomes blue very soon, and then the colour fades again; in presence of molybdic acid, the blue is produced at once and is permanent. When heated with soda lime, a body is formed, subliming in leaflets, easily soluble in ether, and giving a blue coloration with sulphuric acid and molybdic acid, but no coloration with nitric acid. It undergoes a change when heated to  $160^{\circ}$ .

Its hydrochloride is amorphous; the platinumchloride forms an amorphous, light yellow precipitate, which loses water at  $130^{\circ}$ , and then has the composition  $(C_{18}H_{24}N_2O_2HCl)_2PtCl_4$ . The aurochloride is a dirty brown amorphous body. Its oxalate crystallises from alcohol as a white powder, consisting of microscopic needles. The sulphate crystallises from alcohol in stellate grouped white needles, is easily soluble in water and hot alcohol, sparingly in cold alcohol, and insoluble in ether. Dried at  $100^{\circ}$ , it has the formula  $(C_{18}H_{24}N_2O_2)_2H_2SO_4$ . By means of the aqueous solution of the sulphate, the author has tested the delicacy of its reactions with several bodies, and finds that the alkaloid is most easily precipitated by ammonia and soda, whereas the reaction with phosphotungstic acid is not very delicate.

*Pereirine*,  $C_{19}H_{24}N_2O$ .—This alkaloid, obtained as described above, is purified by dissolving it in acetic acid and boiling with animal charcoal; from the yellow solution obtained, ammonia gives a white amorphous precipitate, which, when air-dried, is a greyish-white powder. It is easily soluble in alcohol, ether, and chloroform; also in dilute acids, from which latter it is precipitated by alkalis. Concentrated sulphuric acid dissolves it with a violet-red colour, and nitric acid with a purple-red. It melts at  $124^{\circ}$  to a red mass. Its sulphate and hydrochloride are amorphous, and easily soluble in alcohol. Its platinumchloride is a yellowish-grey amorphous precipitate, having the composition  $(C_{19}H_{24}N_2OHCl)_2PtCl_4 + 4H_2O$ .  
P. P. B.

**Protein Compounds.** By A. STUTZER (*Ber.*, 13, 251).—In this preliminary notice the author states that he has successfully applied cupric hydrate, recommended by Ritthausen for the precipitation of dissolved protein compounds, to the quantitative estimation of such bodies, and their separation from other nitrogenous substances occurring in plants, such as amygdalin, solanine, leucine, tyrosine, asparagine, alkaloids, mustard-oils, nitrates, and ammonia salts.

Further, that protein bodies yield two classes of compounds when acted on by acid gastric juice (pepsine and hydrochloric acid). On the one hand there are formed the decomposition products already known (peptones, acid albuminates, &c.); whilst on the other a *perfectly definite part* of the protein body is absolutely indigestible. This contains nitrogen and phosphorus, and appears to be allied to nuclein.

Ch. B.

**Albuminoids of Various Oily Seeds.** By H. RITTHAUSEN (*Pflüger's Archiv.*, 21, 81—104).—The author, referring to his previous investigation on the constitution of gliadin, 1864, and conglutin, 1868, and the large proportion of nitrogen they contain (18.06 per

cent. and 18·4 per cent. respectively) as compared with albumin, remarks that since that time his results have been confirmed by others and himself. He then gives the details of investigations on the seeds of *Arachis hypogæa* (earth-nut), *Helianthus annuus* (sunflower), *Sesamum indicum*, cocoa-nut, *Brassica napus* (rape), and potatoes.

The methods used were three.

(1.) Extraction with water, to which a small quantity of potash was added (4 grams in 2·5 litres), and subsequent precipitation by acetic or sulphuric acid, washing with water, alcohol, and ether, and drying over sulphuric acid.

(2.) Extraction with dilute lime or baryta water.

(3.) Extraction with 10 per cent. sodium chloride solution (solutions of  $\text{NH}_4\text{Cl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{MgCl}_2$  appear to answer equally well).

From these experiments, the author concludes that the albuminoids obtained by the use of either dilute potash, baryta, or lime water, present no appreciable differences from those obtained by the solutions of the various salts above mentioned, and he thinks that there is no doubt that the hydrates of the alkalis and alkaline earths act on these bodies like a base on an acid, forming compounds readily soluble in water, and that they are precipitated unchanged by neutralisation with an acid.

There appear to be two albuminoids; one containing more than 18 per cent. of nitrogen and one less; the former is found alone in almonds, earth-nuts, para-nuts, pumpkin and sunflower seeds; whilst in castor-oil seeds, sesamum, and cocoa-nut, both occur, but not in rape seeds.

The albuminoids rich in nitrogen, so far as investigated (with the exception of gliadin and the albuminoids found in para-nuts), contain less carbon than animal albumin and casein by 1·5 to 2 per cent.; gliadin and the albuminoids of para-nuts always 1 per cent. This, with the fact that they contain more than 2 per cent. more nitrogen, will serve to distinguish these bodies from animal albuminoids. The sulphur varies considerably, *e.g.*, from 0·55 per cent. in earth-nuts to 1·3 per cent. in sesamum. Compare the difference between the conglutin of lupins, which contains 0·91 per cent. of sulphur, and that of almonds, which contains 0·45 per cent. Lastly, he draws attention to the close relation between the bodies obtained by the methods above mentioned, and conglutin from lupines and from almonds.

W. N.

## Physiological Chemistry.

### Changes which Starch undergoes in the Animal Organism.\*

By E. H. BIMMERMANN (*Pflüger's Archiv.*, 20, 201—210).—The author, after referring to the statement of Musculus and Gruber, that starch

\* Conf. Musculus and O'Sullivan, *Journ. Chem. Soc.*, 1872—76; T. H. Brown and J. Heron, *Journ. Chem. Soc.*, Sept., 1879; Roberts, *Lumleian Lectures*, 1880; Maly, *Jahresbericht Thier. Chem.*, 1878, pp. 49—54.



by the action of diastase or acids, yields soluble starch, maltose, grape-sugar, and three forms of dextrin, named respectively  $\alpha$ ,  $\beta$ , and  $\gamma$  achroodextrin, which are variously affected by ferments, proceeds to state that while maltose and grape-sugar are produced by the action of saliva on starch, glycogen, whether obtained on a diet of grape-sugar or albuminoids, when treated in the same manner, yields larger quantities of maltose and grape-sugar, and a reducible dextrin. Sachsse's method of estimating sugar by mercuric iodide was used, as it was found difficult to determine the end of the reaction with Fehling's solution. The substances were injected into the jugular vein of a rabbit, and the urine subsequently examined, with the following results:—

Maltose is partly converted in the blood into grape-sugar, and partly passes out unchanged. Soluble starch yields dextrin and grape-sugar. Achroodextrin ( $\alpha$ ) suffers only partial change, grape-sugar and maltose being found in the urine, together with dextrin. Achroodextrin ( $\beta$ ) yields a similar result. Achroodextrin ( $\gamma$ ) yielded no sugar. Generally, the results tend to show that the changes which starch undergoes in the body are similar to those which occur when it is submitted to the action of diastase outside it. W. N.

## Chemistry of Vegetable Physiology and Agriculture.

**Comparative Value of Soluble and Insoluble Phosphates.** By A. VOELCKER (*Jour. Roy. Agri. Soc.*, 1880, 152—159).—This is a summary of the comparative results obtained in early field experiments by applying bones and other phosphates alone and after previous treatment with sulphuric acid, showing the advantage of the latter method. R. W.

**Analyses of Manures and of Cattle Foods.** By A. VOELCKER (*Jour. Roy. Agri. Soc.*, 1880, 311).—The guano from Pabillon de Pica is richer in ammonia than that from Huanillos, which is again much more valuable than that from Lobos de Afuera and Lobos de Tierra. Three samples of commercial soot contained 2.35, 3.63, and 5.04 per cent. of nitrogen; the second was of about average quality. An unusually rich sample of bats' guano contained 8.92 per cent. of nitrogen, and 5.02 per cent. of phosphoric acid.

Rice meal consists chiefly of the external layers of rice, which are separated in dressing. The mean of five analyses was as follows:—

| Water. | Albuminoids. | Fat.  | Carbohydrates. | Fibre. | Ash.  |
|--------|--------------|-------|----------------|--------|-------|
| 11.46  | 12.47        | 11.61 | 49.66          | 6.79   | 8.00  |
|        |              |       |                |        | R. W. |

## Analytical Chemistry.

**Vapour-density Determinations in the Vapour of Phosphorus Pentasulphide.** By W. KNECHT (*Annalen*, 202, 31—36).—Graebe (*Ber.*, 11, 1646), in using Meyer's method with Wood's metal, calculated the sp. gr. of this alloy at 530° (the boiling point of phosphorus pentasulphide as determined by Hittorf, *Pogg. Ann.*, 126, 193), to be 9.051. The author has determined the sp. gr. of the alloy directly, and finds it to be 9.06 at 530°, and also that its coefficient of expansion is constant between 100° and 580°. Further, the alloy is not attacked by phosphorus pentasulphide, and in using the latter the vessels may be easily freed from it by cooling down to 100°, and then suspending them for some time in a vessel containing boiling water. The author has determined the vapour-densities of the following bodies in the vapour of phosphorus pentasulphide, and finds their densities are such as required by theory, viz., triphenylbenzene (10.51), isodinaphthyl (8.865), dinaphthylketone (9.07), and tetraphenylethane (11.65).  
P. P. B.

**Modification of Zulkowsky's Apparatus for the Volumetric Estimation of Nitrogen.** By E. LUDWIG (*Ber.*, 13, 883—885).

**Determination of Nitrogen.** By H. SCHIFF (*Ber.*, 13, 885—887).—A simpler and more convenient form of the apparatus described by Schwarz for estimating nitrogen by Dumas' method (*Ber.*, 13, 771) was invented by the author in 1868.  
W. C. W.

**Estimation of Gold and Silver by Quartation with Cadmium.** By F. KRAUS (*Dingl. polyt. J.*, 236, 323—326).—Balling (*Oestreichische Zeitschr. f. Berg. und Huttenwesen*, 1879, 597) describes a modification of Güptner's method of separating gold by quartation with zinc, in which cadmium is used instead of zinc, the fusion of the metals being made under a layer of potassium cyanide. The author has subjected this method to a close investigation, and has more especially compared it with the methods usually employed in mints for the determination of alloys of gold and silver. His results seem to show that Balling's method is simpler and more readily carried out than the cupellation method, and he strongly recommends chemists and assayers to investigate it more minutely. Moreover, the circumstance that the silver can be determined by Volhard's method in the decanted acid solution and in the washings, gives it an advantage over the process by cupellation.  
D. B.

**Detection of Water in Alcohol and Ether.** By C. MANN (*Dingl. polyt. J.*, 236, 430; and *Chem. Zeitung*, 1880, 307).—Mix 2 parts citric acid and 1 part of molybdic acid; heat until incipient fusion, and warm with 40 parts of water. Filter-paper dipped in this and dried at 100° is blue. In alcohol or ether free from

water, the colour remains unchanged, but if water be present the paper will lose its colour, especially if warmed. J. T.

**Analysis of Wine.** By V. WARTHA (*Ber.*, 13, 657—662).—In order to detect the presence of rosaniline compounds in red wine, the three following tests must be employed :—

(1.) 20 c.c. of the wine are mixed with an excess of magnesium oxide in a test-tube, and then a mixture of equal parts of colourless amyl alcohol and ether, gradually added with frequent shaking. On standing, the supernatant liquid becomes rose-coloured, even if the wine contains only 1 mgrm. of rosaniline per litre. With strongly coloured southern wines containing only a small quantity of rosaniline, the colour is sometimes yellowish or a bright brown.

(2.) 20 c.c. of the wine are shaken with 10 c.c. of lead acetate solution (official strength) and filtered into a dry test-tube. If a moderate quantity of rosaniline be present, the filtrate is rose-coloured; whereas if there is only a small quantity of rosaniline or aniline-violet the liquid is either colourless or only slightly yellow. In either case 1 c.c. of the above mixture of amyl alcohol and ether is added, the liquid shaken, and allowed to stand; the upper layer of liquid then becomes rose-coloured if rosaniline be present.

(3.) Evaporation is unnecessary if tests (1) and (2) have indicated the presence of a considerable quantity of the dye. If, however, this is not the case, 150—200 c.c. of the wine are quickly evaporated over a naked flame to one-fourth of their original bulk, and the *hot* liquid poured into a stoppered glass cylinder (previously cleansed with strong nitric acid and water), and excess of ammonia added, and the liquid carefully shaken with 30—40 c.c. of pure ether. The ethereal solution is then passed through a dry filter into a porcelain basin containing one or two threads (3—4 cm. long) of Berlin wool previously washed and dried; the ether is allowed to evaporate spontaneously in a warm place, when the wool becomes dyed rose-coloured if rosaniline be present. This is further confirmed by dividing one of the threads into two parts, one of which is moistened with strong hydrochloric acid, and the other with strong ammonia, when the colour must be replaced in both cases by yellow if rosaniline, and by green if aniline-violet be present. By this means .01 mgrm. of rosaniline can be detected in 1 litre of wine.

Sulphurous acid is frequently used for bleaching the so-called Schiller wines, a process which otherwise takes place only very slowly. As sulphurous acid not only destroys the peculiar flavour of many of these wines, but has also a deleterious physiological effect, it is important to be able to detect the presence of this acid in such wines. For this purpose 50 c.c. of the wine are gently distilled until about 2 c.c. have passed over. A few drops of a neutral solution of silver nitrate are then added to the distillate which becomes opalescent if it contains sulphurous acid. To prove the absence of a chloride, a little nitric acid is added; the liquid should become quite clear. The distillate also decolorises iodide of starch and potassium permanganate. The latter reagents may also be used when a quantitative determination is required.

The author states that sulphurous acid present in wines only oxidises very slowly, sometimes taking many years.

T. C.

**Estimation of Urea by Sodium Hypobromite.** By C. MEHU (*Bull. Soc. Chim.* [2], 33, 410—415).—The recent experiments of Jay (*ibid.* [2], 33, 102 and 105) have confirmed the author's statement, that in presence of cane-sugar and glucose the quantity of nitrogen evolved from urea by the action of sodium hypobromite, is increased by 7 to 7.7 per cent., *i.e.*, that approximately the theoretical yield of nitrogen is obtained. Neither cane-sugar nor glucose by itself causes any evolution of gas from sodium hypobromite; on the other hand, sodium hypobromite solution, soon after its preparation, becomes saturated with free oxygen, and the addition of cane-sugar or glucose prevents or greatly retards the evolution of this gas. The actual observed deficiency of nitrogen when working with pure urea and hypobromite varies from 8 per cent., which is the constant number obtained under the most favourable conditions, to 15 per cent., when very dilute solutions of urea are employed, and the temperature is about 0° C. An addition of sugar to normal urine causes an increase in the nitrogen evolved of 3—5 per cent., rarely more. The increase is greater with urine containing little extractive matter, very slight when the urine is charged with blood, pus, &c., or has begun to putrefy. With diabetic urine containing not less than 60 grams of glucose to 10 grams of urea, the yield of nitrogen is scarcely increased by adding sugar. It has been long recognised that in working with normal urine, the deficiency of nitrogen is less than it would be with a solution containing the same quantity of pure urea. This compensation, which it is not easy to estimate accurately, has been attributed to nitrogen disengaged by the hypobromite from creatinine, uric acid, and other nitrogenous substances. Considering that the weight of uric acid present is rarely more than one-fiftieth that of the urea, and that of the creatinine about one-sixty-fifth of the urea, and that these compounds yield only one-half and two-thirds their nitrogen by the action of sodium hypobromite, the author concludes that the greater part of the compensation cannot be due to this source, but thinks it probable that the extractive matter present acts like sugar in increasing the yield of nitrogen from urea. To render the results obtained with saccharine urine comparable with those obtained with normal urine, the author recommends that in all cases cane-sugar be added to the amount of ten times the weight of the urea present. The difference between the actual and theoretical yield of nitrogen will then not exceed 1 per cent.

J. M. H. M.

**Quantitative Estimation of Urea.** By E. PFLÜGER (*Pflüger's Archiv.*, 21, 248—286).—In this paper the author, after discussing various objections which have been made to Liebig's method, states that he has found a possibility of error to the extent of 14 per cent., but believes that the method yields good results if Liebig's directions with certain modifications are carefully carried out. He first describes a method of preparing a pure urea from the commercial article, and also a method of preparing a pure mercuric nitrate solu-

tion. He then gives a number of experiments demonstrating the accuracy of his solutions, and shows that the manner in which the neutralisation is carried out affects the result very materially. For neutralisation, he uses a soda solution, and remarks that when baryta-water is used for neutralisation more mercury solution is required to give the colour reaction than with soda.

If the mercury and soda solutions are run into the urea solution alternately and in small quantities at a time, the reaction is reached too soon, *e.g.*, at 17.2 to 17.3 c.c., instead of 20 c.c.

If the whole quantity of mercury solution required be added as nearly as possible at once, very accurate results are obtained. The time allowed to elapse between the adding of the mercury solution and neutralisation is also important; if too long, the reaction comes too early. Experiments are given tending to show that mercuric nitrate forms more than one compound with urea.

The author then describes his own method of carrying out Liebig's process. The solutions required are the usual mercury solution and a soda solution of known strength, the quantity of which required to neutralise a known volume of the mercury solution has been accurately ascertained.

For testing, he uses a plate of colourless glass on black cloth: the mercury solution is then run in, and the sodium carbonate test applied on the glass plate, the drops being stirred each time until the yellow colour, which at first disappears on this treatment, becomes permanent; then neutralises.

The experiment is then to be repeated, the mercury solution being run in quickly up to the point indicated by the trial experiment, neutralised at once with the standard sodium solution and tested as before.

The author's correction for concentration differs somewhat from that given by Liebig. Pflüger's rule is: given the volume of urea solution + the volume of soda solution necessary for neutralisation, + the volume of any other fluid free from urea which was added and call this  $V_1$ ; call the volume of mercury solution used  $V_2$ , then the correction  $C$  is:

$$C = - (V_1 - V_2) \times 0.08.$$

Examples are given for solutions of urea of 1 per cent., 0.5 per cent., 0.33 per cent., 0.25 per cent., showing that this formula will hold so long as the mixture is less than three times the volume of mercury solution used.

Experiments are given on strong solutions with the same result. The necessity of adding nearly all the mercury solution at once is again dwelt upon, elaborate directions are then given for preparing the mercury and soda solutions (sodium carbonate of 1.053 sp. gr. is recommended), and in conclusion the author states that if the sulphates, phosphates, and chlorides be removed, and the precautions stated are used, the method gives excellent results with urine.

W. N.

**Commercial Valuation of Bituminous Rocks and Limestones.** By P. KIENLEN (*Bull. Soc. Chim.* [2], 33, 459—461).—A

stout glass tube, about 50 cm. long and 25 mm. diameter, is fitted at one end with a cork, the other end is blown out to a bulb, below which the tube is drawn out and furnished with a glass stopcock. The bulb is packed with asbestos or glass wool well washed and ignited, and 10 grams of the finely-powdered rock are introduced in alternate layers with pounded glass, so that the tube is about two-thirds filled. 50 c.c. of a mixture of equal volumes of carbon bisulphide and benzene are now added, and the tube is allowed to stand for an hour, when the strongly coloured liquid is drawn off and the treatment repeated until the extract is no longer coloured. Three digestions in the cold of one hour each are usually sufficient. The volatile liquid is carefully distilled off in a weighed flask, the residue dried in a current of air at the ordinary temperature and weighed. Some bituminous limestones from Lobsann (Alsace) contained 12–16 per cent. of bituminous matter, whilst some volcanic rocks from the Auvergne contained nearly 24 per cent. Sulphur may be estimated by fusing the finely-powdered rock in a porcelain crucible with 4 parts potassium nitrate, 4 parts sodium carbonate, and 2 parts sodium chloride, extracting with water, acidifying with hydrochloric acid, and precipitating by means of barium chloride. C. H. B.

**Analysis of Heavy Mineral, Resin, and Fatty Oils, and of Resin in Commercial Oils (Part I).** By A. RÉMONT (*Bull. Soc. Chim.* [2], 33, 461–466).—The oils used for lubrication, currying, &c., may be divided into two classes: 1, non-saponifiable; 2, saponifiable.

*Non-saponifiable.*—*Heavy mineral oils*, consisting mainly of saturated hydrocarbons, are not acted on by alkalis, and are but slightly attacked by acids. They have an amber colour, are dichroic, appearing bluish-green by reflected light, exert no action on polarised light, and are very slightly soluble in alcohol: sp. gr. = 0.850 to 0.920. When purified they have little or no smell at ordinary temperatures, but on warming them a petroleum odour is readily perceived. At a high temperature, the oil darkens and evolves vapours which burn with a bright smokeless flame. When distilled, very little passes over below 300°, the greater portion distilling between 300° and 360°: in the case of very heavy oils, a considerable residue remains even at 360°.

*Resin oils*, obtained by distilling inferior kinds of resin with lime, consist of hydrocarbons of the benzene and terebenthene series, together with bodies allied to the phenols, and are slightly attacked by alkalis. Nitric acid is without action in the cold, but if warmed a violent reaction ensues, nitrous fumes are evolved, and a semifluid mass is formed, which, when washed with water and cooled, yields a brittle solid, soluble in alcohol. With sulphuric acid, they are blackened at ordinary temperatures: when heated, sulphurous anhydride is given off, but the oil never completely dissolves. These oils have a characteristic odour, and are somewhat more soluble in alcohol than the preceding group: sp. gr. = 0.960 to 0.990. They have a brownish-yellow colour, are dichroic and generally possess a dextrorotatory power of about + 30°; in only one case out of fifteen was a levorotatory power of  $\alpha_D = -8^\circ 24'$  observed. Stannic chloride produces a

characteristic violet colour, which requires some time for its development. When distilled, a portion passes over below  $250^{\circ}$ , a considerable quantity below  $300^{\circ}$ , and almost the whole below  $360^{\circ}$ . The vapour burns with a very smoky flame.

*Saponifiable.*—*Fatty acids*, generally of the oleic series, are sometimes mixed with oils. They are usually liquid at ordinary temperatures, have a characteristic odour which becomes more marked as the temperature rises, have a faintly acid reaction, and are readily soluble in solutions of soda, alkaline carbonates, borax, and sodium silicate. Oleic acid is soluble in all proportions in alcohol, even if moderately dilute: a large excess of the solvent causes a slight turbidity which, if due to pure oleic acid, disappears on the addition of a few drops of hydrochloric acid. When strongly heated, these acids give off highly inflammable acrid vapours, which burn with a slightly smoky flame. Sp. gr. =  $0.900$ — $0.905$ .

*Fatty oils*, usually of animal origin, dissolve, after boiling for some time, in alkaline solutions; on the addition of an excess of caustic soda, or better of common salt, the soap separates out completely. When heated at  $100$ — $110^{\circ}$  with 7 or 8 per cent. of sulphuric acid of  $66^{\circ}$  B. they are completely saponified: the fatty acid may be isolated by washing with a large quantity of boiling water. They are slightly soluble in cold, but dissolve completely in hot alcohol, and, like the fatty acids, have no action on polarised light. Sp. gr.  $0.910$ — $0.945$  according to origin.

*Resin or Colophony*, sp. gr.  $1.070$ , derived from the cedar or pine, is sometimes dissolved in oils in order to increase their density. It has a brownish-yellow colour, and dissolves easily in moderately strong alcohol; the solution has a mean rotatory power of  $[\alpha]_D = +15^{\circ}$ . Like the oils, it is readily soluble in carbon bisulphide, chloroform, benzene, ether, and light petroleum. It is easily saponified by solutions of alkalis, alkaline carbonates, and borax. Resin soap is not completely precipitated by either caustic soda or common salt, about 20 per cent. remaining in solution. C. H. B.

**Detection of Coal-Gas in Earth.** By E. KÜNIGS (*Dingl. polyt. J.*, 236, 430).—In some excavations at Crefeld the earth had an unmistakable odour of coal-gas. The author (*Corr-blatt Ver. Anal. Chem.*, 1880, 59), treated 6 litres with sulphuric acid, and passed steam into the vessel. In the first distillate, naphthalene could be detected.

J. T.

## General and Physical Chemistry.

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**Measurement of the Actinism of the Sun's Rays and of Day-light.** By R. A. SMITH (*Chem. News*, 41, 211—212).—The process depends on the fact that potassium iodide acidified with dilute nitric, or preferably sulphuric acid, undergoes little or no change in the dark, but on exposure to light gives off iodine, the amount of which may be readily and exactly determined by thiosulphate. Potassium bromide may be substituted for the iodine, but it is less delicate.

F. L. T.

**Relative Intensity of the Spectral Lines of Gases.** By J. R. CAPRON (*Phil. Mag.* [5], 9, 329—330).—The author refers to experiments described in his "Auroræ and their Spectra." Geissler tubes containing various gases were gradually moved farther away from the slit of the spectroscope, when it was found that the colours of the spectrum disappeared in the order—red, yellow, violet, green. Hence the brighter lines of a spectrum may be seen singly as a matter of intensity, independently of other causes, such as temperature or pressure.

C. H. B.

**Bright-line Spectrum of Scandium.** By R. THALÉN (*Compt. rend.*, 91, 45—48).—The spectrum of scandium, as obtained by passing a powerful induction spark between aluminium poles moistened with a solution of the chloride, is very complicated, and contains more than a hundred lines. All the lines, which are very characteristic, are fine, with the exception of some in the yellow and orange, and seven strong lines in the blue-violet. A line at 4374 is slightly more refrangible than a prominent yttrium line, with which it might be confounded. Some very faint bands, situated at 5900—5730, are probably due to the oxides, as are possibly also the broad lines in the blue-violet at 6193—6016. A table is given showing the wave-lengths of the lines in decimeters. The chloride was prepared partly by Nilson from euxenite and partly by Cleve from gadolinite and keilhanite. Both samples gave absolutely identical spectra.

C. H. B.

**Relations between the Physical Properties of Bodies and their Chemical Constitution.** By J. W. BRÜHL (*Ber.*, 13, 1119—1130).—The statement made in a previous communication (*Ber.*, 12, 2135, this vol., 293) that variations in atomic refraction can occur in the case of multivalent elements only, whilst those of univalent elements are constant in all cases, has been abundantly confirmed by a large number of experimental determinations. The following are the mean atomic refractions obtained:—

|  |       |
|--|-------|
| $r_a O''$ (the oxygen doubly combined with the same carbon-atom) .....                           | = 3·4 |
| $r_a O'$ (the oxygen united with the same carbon-atom by only one of its combining powers) ..... | = 2·8 |
| $r_a H = 1·3$ ; $r_a C' = 5·0$ ; $r_a Cl = 9·88$   |       |



Or for a ray of infinite wave-length  $A_1$ —

$$\tau_A O'' = 3.29; \tau_A O' = 2.71; \tau_A H = 1.29; \tau_A C' = 4.86.$$

T. C.

**Determination of Chemical Affinity in Terms of Electromotive Force Part II.** By C. R. A. WRIGHT and E. H. RENNIE (*Phil. Mag.* [5], 9, 331—347).—*Decomposition of Water.*—The current from a Daniell battery was passed through a voltmeter placed in a calorimeter, and the average difference of potential between the plates of the voltmeter was determined by means of a quadrant electrometer. The E.M.F. representing the amount of work corresponding to the sum of the chemical and physical changes was calculated from the formula

$$e = E - \frac{ha\chi J}{n}$$

where  $a$  = equivalent of the electrolyte,  $h$  = the heat developed in the voltmeter, and  $n$  = the amount of decomposition in grams. The water-value of the calorimeter and the corrections for radiation were determined with the greatest possible care.

In the case of water acidulated with 22 per cent.  $H_2SO_4$  the mean value of  $E - \frac{h}{n}a\chi J$  for 18 experiments, with varying battery power and time, was  $1.5000 \times 10^8$ . Corrections were introduced for the heat absorbed by the vaporisation of the water carried away by the evolved gases and the work necessary to separate the water decomposed from the sulphuric acid.

A series of experiments made by the authors tends to show that the value of  $J$ , as determined by Joule in 1867 by the electric current method, is about 0.5 per cent. too low, owing to three sources of error, viz., the higher mean temperature of the wire compared with that of the calorimeter, the increased resistance of the wire caused by the coating of varnish applied to it, the greater heating of the B.A. unit-coil, the wires of which were imbedded in solid paraffin, compared with the experimental wire which was placed in water. The experiments also show that where a current has to be passed through a wire for any length of time an error will be caused by the increased resistance of the wire due to its being heated to a temperature above that of the medium in which it is placed.

C. H. B.

**Constant and Powerful Voltaic Pile.** By E. REGNIER (*Compt. rend.*, 90, 1550—1553).—The zinc plate, which need not be amalgamated, is placed in a solution of caustic soda, and the copper plate in a solution of copper sulphate, the two liquids being separated by a diaphragm made of several thicknesses of parchment paper, which are folded so as to form a rectangular inner cell. The resistance of the solutions is diminished by the addition of suitable salts, so that the total resistance of the cell is about 0.075 ohm. The E.M.F. varies from 1.3 to 1.5 volt, according to the strength of the solutions. By means of a current from a magneto-electric machine the various substances may be regenerated and used again in the cell. This indirect

transmission of the electricity produced by machines may in some cases be more advantageous than direct transmission. C. H. B.

**Determination of the Specific Electrical Resistance of Certain Copper-Tin Alloys.** By O. J. LODGE (*Phil. Mag.* [5], 8, 554—558).—The following table gives the percentage composition, specific resistance in square centimeters per second, and conductivity of a centimeter cube in B.A. units of the six alloys examined.

|        | Cu.  | Sn.   | Resistance. | Conductivity. |
|--------|------|-------|-------------|---------------|
| A .... | 19.2 | 80.8  | 12960       | 77100         |
| B .... | 61.8 | 38.2  | 10960       | 91200         |
| C .... | 68.3 | 31.7  | 47660       | 21000         |
| D .... | 0.0  | 100.0 | 11830       | 84500         |
| E .... | 87.4 | 12.6  | 17090       | 58500         |
| F .... | 90.3 | 9.7   | 15270       | 65500         |

The curve representing these results agrees very well with the induction balance curve obtained by W. C. Roberts (this vol.), but does not so closely resemble the curve representing the conductivity for heat of similar alloys as determined by Matthiessen. The abnormal behaviour of the alloy C ( $\text{SnCu}_4$ ) is worthy of notice. C. H. B.

**Analogy between the Conductivity for Heat and the Induction Balance Effect of Copper-Tin Alloys.** By W. C. ROBERTS (*Phil. Mag.* [5], 8, 551—553).—The curve representing the action of copper-tin alloys on the induction balance, as determined by the author, is very similar to that representing the conductivity for heat of a similar set of alloys, as determined by Calvert and Johnson, the critical points being practically the same on both curves. The alloys occupying the critical points on the induction balance curve are respectively  $\text{SnCu}_4$ , a speculum metal, having a yellow-grey tint and large conchoidal fracture, and  $\text{SnCu}_3$ , having a blue-grey colour and coarse surface of interrupted crystalline plates. The two alloys pass insensibly one into the other. C. H. B.

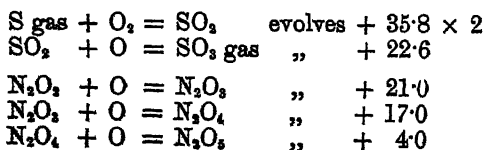
**Freezing Mixtures formed by an Acid and a Hydrated Salt.** By BERTHELOT (*Compt. rend.*, 90, 1191—1195).—The author agrees, on the whole, with Ditte (this vol., p. 602), but points out that in the case of hydrochloric acid and sodium sulphate the maximum thermal effect would correspond with the formation of sodium-hydrogen sulphate and not sulphuric acid. Hydrated sodium sulphate may be regarded as a system in equilibrium composed of the true hydrate, a certain quantity of the anhydrous salt, and free water. When brought in contact with a substance capable of acting on it, such as hydrochloric acid, the latter will first attack the anhydrous sulphate, since no work is required to separate it from combined water. The removal of the small quantity of the anhydrous salt destroys the equilibrium of the system, a fresh quantity is produced, this is immediately acted on by the acid, and so on until the decomposition is complete, since none of the new products bring about special conditions of equilibrium tending to limit the reaction. The liberated water assumes the liquid

condition, thus causing an absorption of heat. In the case of equivalent quantities of hydrochloric acid and sodium sulphate, the end products of the reaction cannot be simply sulphuric acid and sodium chloride, for these two substances react together, forming sodium hydrogen sulphate and hydrochloric acid, corresponding with the maximum thermal effect; and, if there were no decomposition of the products, the reaction would cease, whatever the excess of hydrochloric acid. But the presence of the solvent modifies the reaction, the sodium-hydrogen sulphate is partially decomposed, and a system is formed composed of this salt, the normal sulphate, free sulphuric acid, and water. The sodium chloride produced causes further complications, and the final result is a system composed of water, hydrochloric and sulphuric acids, sodium chloride and sulphate, and sodium-hydrogen sulphate. This system remains in equilibrium under certain limited conditions only. If excess of hydrochloric acid is present, the sodium chloride is thrown out of solution and the equilibrium of the system is destroyed; the anhydrous sulphate is acted on by the hydrochloric acid, more sodium chloride is produced, this is at once thrown out of solution, and so on. The whole of the sodium chloride, is, however, only precipitated and the decomposition thus rendered complete, when the excess of hydrochloric acid added is such that, with the water set free, it forms a hydrate of the composition  $2\text{HCl} \cdot 13-16\text{H}_2\text{O}$ , in which the salt is almost totally insoluble. This explanation holds equally well for the reaction of other acids with other hydrated salts. In all these cases there is first an exothermic action, in accordance with the principle of maximum work. The changes which cause an absorption of heat are dissociation of the hydrated salt; disaggregation by the solvent; solution, which in certain cases plays only an intermediate part; and the liquefaction of the liberated water.

C. H. B.

**Some General Relations between the Chemical Mass of the Elements and the Heat of Formation of their Compounds.** By BERTHELOT (*Compt. rend.*, 90, 1511—1515).—The law expressing the work done by the union of two heterogeneous molecules in terms of their mass, temperature, and distance, is not yet known, and possibly its discovery implies that of the more general function, which includes all simple bodies in one common equation and reduces their different states to multiple forms of the same matter, differing in the mode of grouping of its parts and the nature of their motions. The study of the chemical and physical properties of the elements tends to show that atoms have a complex structure, are endowed with a specific architecture, and have complicated internal motions.

*Multiple proportions.*—When no change of physical state occurs the heat developed by successive combinations of two elements or compounds diminishes as one of the elements accumulates.



|                                     |          |
|-------------------------------------|----------|
| Hg, solid, + Br solid evolves       | + 35.0   |
| HgBr + Br solid                     | „ + 17.6 |
| Hg, solid + I                       | „ + 23.8 |
| HgI + I                             | „ + 11.2 |
| Sn + Br <sub>2</sub> solid          | „ + 68.8 |
| SnBr <sub>2</sub> + Br <sub>2</sub> | „ + 32.2 |

The greater part of the work is done in the first combination of heterogeneous molecules. This does not, however, apply to endothermic combinations, such as the formation of cyanogen, acetylene, or nitrogen monoxide. As a rule, the greater the complexity of the system formed the less its stability.

When a change of state accompanies the chemical change the heat evolved is in many cases proportional to one of the elements and is independent of the other. For example, the heat of formation of amalgams rich in mercury is sensibly equal to the heat of fusion of the mercury; it is almost the same for both potassium and sodium. Again, the heat of formation of KI, from KI and gaseous iodine is equal to the heat of vaporisation of the iodine; similar relations are approximately true in the case of potassium tribromide and the alkaline polysulphides. The heat of formation of complex from simple saline hydrates is approximately equal to the heat of solidification of the water.

*Chemical Functions.*—Carbon compounds having the same function evolve the same amount of heat when undergoing the same transformation. For example, the union of H<sub>2</sub> with a hydrocarbon of the ethylene series develops heat = + 22 cal., the union of a gaseous haloid acid with the same hydrocarbons gives + 15 cal., the combination of O with an aldehyde to form an acid gives + 73 cal. Isomerides of the same function evolve very slight quantities of heat when undergoing reciprocal transformations; if, however, the function changes a considerable development of heat takes place. A relation which is too well marked to be accidental can be traced between the atomic weights and the heat of formation of the binary compounds of nickel, cobalt and iron, calcium and strontium, thallium and lead, platinum and palladium, chlorine, bromine, and iodine. A large number of elements, however, show very different relations. C. H. B.

**Thermo-chemistry of the Oxides of Nitrogen.** By J. THOMSEN (*Ber.*, 13, 1093—1095).—A comparison of the numbers obtained by the author (*ibid.*, 13, 428) with those of Berthelot (*Compt. rend.*, 90, 779). T. C.

**Thermo-chemical Study of the Alkaline Polysulphides.** By P. SABATIER (*Compt. rend.*, 90, 1557—1560).—*Potassium Polysulphides.*—The tetrasulphide, K<sub>2</sub>S<sub>4</sub>·2H<sub>2</sub>O, is obtained in large red deliquescent crystals by dissolving 3 atoms of sulphur in a solution of the monosulphide. The solution of 1 equivalent in at least 250 H<sub>2</sub>O at 12° caused absorption of heat = -7.5 cal. The preceding compound effloresces in a vacuum, leaving K<sub>2</sub>S<sub>4</sub>·H<sub>2</sub>O. The solution of 1 equivalent in 100 parts H<sub>2</sub>O at 11.3°, caused absorption of heat = -2.24 cal.

A red, translucent, anhydrous tetrasulphide,  $K_2S_4$ , is obtained by heating the monohydrate below a dull red heat in a current of hydrogen. The solution of 1 equivalent in water at  $15.7^\circ$  developed heat = + 1.2 cal. A dilute solution of the tetrasulphide was decomposed by hydrochloric acid in presence of an excess of iodine dissolved in potassium iodide, and the heat developed was measured, the necessary corrections being introduced for the specific heat of the iodine solution, and the heat absorbed in its formation. The various calorimetric determinations gave the following results:—

*Heat of Formation.*

|                                |   |                          |              |
|--------------------------------|---|--------------------------|--------------|
| $K_2 + S_4$ solid              | = | $K_2S_4$ dissolved, gave | + 117.8 cal. |
| $K_2 + S_4$ „                  | = | $K_2S_4$ anhydrous „     | + 116.6 „    |
| $K_2S$ dissolved + $S_2$ solid | = | $K_2S_4$ dissolved „     | + 5.2 „      |
| $K_2S$ anhydrous + $S_2$ „     | = | $K_2S_4$ anhydrous „     | + 12.4 „     |

*Heat of Hydration.*

|                              |   |                                   |                     |
|------------------------------|---|-----------------------------------|---------------------|
| $K_2S_4$ anhydrous + $H_2O$  | = | $K_2S_4 \cdot H_2O$ (solid water) | evolves + 2.66 cal. |
| $K_2S_4$ „ + $2H_2O$         | = | $K_2S_4 \cdot 2H_2O$ „            | + 5.76 „            |
| $K_2S_4 \cdot H_2O$ + $H_2O$ | = | $K_2S_4 \cdot 2H_2O$ „            | + 3.10 „            |

*Sodium Polysulphides.*—The tetrasulphide,  $Na_2S_4$ , is obtained as a red, translucent substance by cautiously fusing the monosulphide with sulphur in an atmosphere of hydrogen. The solution of 1 equivalent in 600  $H_2O$  at  $16.5^\circ$  developed heat = + 9.8 cal. The author was unable to obtain the crystallised tetrasulphide described by Schone. The various polysulphides were obtained in solution by dissolving as much sulphur as possible (3.6 equivalents) in a solution of the monosulphide, and then mixing this solution with the requisite proportion of monosulphide. Calorimetric determinations, made in the same way as in the case of the potassium compounds, gave the following results:—

*Heat of Formation from Elements.*

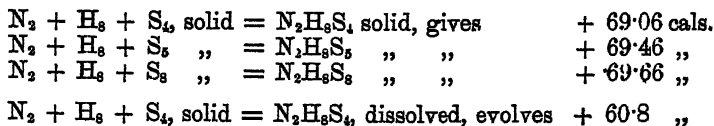
|                    |   |                           |              |
|--------------------|---|---------------------------|--------------|
| $Na_2 + S_4$ solid | = | $Na_2S_4$ dissolved, gave | + 108.2 cal. |
| $Na_2 + S_3$ „     | = | $Na_2S_3$ „               | + 106.4 „    |
| $Na_2 + S_2$ „     | = | $Na_2S_2$ „               | + 104.6 „    |
| $Na_2 + S_4$ „     | = | $Na_2S_4$ anhydrous „     | + 98.4 „     |

*Heat of Formation from the Monosulphide.*

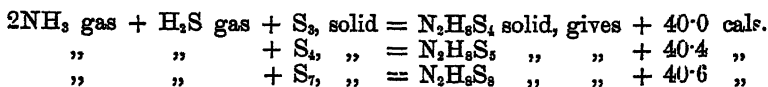
|                                 |   |                           |             |
|---------------------------------|---|---------------------------|-------------|
| $Na_2S$ anhydrous + $S_2$ solid | = | $Na_2S_4$ anhydrous, gave | + 10.2 cal. |
| $Na_2S$ dissolved + $S_2$ „     | = | $Na_2S_4$ dissolved „     | + 5.0 „     |
| $Na_2S$ „ + $S_2$ „             | = | $Na_2S_3$ „               | + 3.2 „     |
| $Na_2S$ „ + $S$ „               | = | $Na_2S_2$ „               | + 1.4 „     |

The solution of each successive equivalent of sulphur in the monosulphide develops heat = + 1.8 cal.; this value is the same in the case of potassium. C. H. B.

**Thermo-chemical Study of Ammonium Polysulphides and Hydrogen Persulphide.** By P. SABATIER (*Compt. rend.*, 91, 51—54).

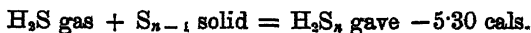
*Ammonium Sulphides.*

The composition of each atom of sulphur above the tetrasulphide causes no sensible evolution of heat.



Dry ammonia and dry hydrogen sulphide in presence of solid sulphur combine to form a certain proportion of polysulphide.  $\text{N}_2\text{H}_8\text{S}_8$  was obtained in red crystals by the action of the mother-liquor from the pentasulphide, on sulphur. Fritzsche assigned to it the composition  $\text{N}_2\text{H}_8\text{S}_7$ .

*Hydrogen Persulphide.*—Obtained by the action of hydrochloric acid on calcium polysulphide. Its composition varied between  $\text{H}_2\text{S}_8$  and  $\text{H}_2\text{S}_{10}$ . This substance acts very slowly on a solution of iodine; it was therefore decomposed by means of solid hydrated sodium sulphide.



C. H. B.

**Behaviour of Carbonic Anhydride in relation to Pressure, Volume, and Temperature.** By R. CLAUSIUS (*Ann. Phys. Chem.* [2], 9, 337—358).—The author discusses the several formulæ which have been proposed by Rankine, Hirn, Recknagel, and Van der Waals, for expressing the relations between the pressure, temperature, and volume of gases, which, like carbonic acid, depart from Marriotte's law. He has himself investigated an expression for these relations, and has arrived at this formula

$$p = R \frac{T}{v - \alpha} - \frac{c}{T(v + \beta)^2}$$

where  $p$  represents the pressure,  $v$  the volume, and  $T$  the absolute temperature, while  $R$ ,  $c$ ,  $\alpha$ , and  $\beta$  are constants. Taking one atmosphere as the unit of pressure, and the volume of the gas at  $0^\circ$  under 760 mm. as the unit of volume, the following are the values of the constants of the formula for carbonic acid gas:— $R = 0\cdot003688$ ;  $c = 2\cdot0935$ ;  $\alpha = 0\cdot000843$ ;  $\beta = 0\cdot000977$ . On comparing this formula with the results obtained by Andrews in three recent and in three older series of experiments on carbonic acid, the author finds the most satisfactory agreement between the observed and the calculated values of  $p$ , except only where the pressure amounts to 400 or 500 atmospheres; and, for reasons explained in the paper, he considers that the divergences are more probably due to errors of experiment than to failure of the formula.

R. R.

**Suggestion as to the Constitution of Chlorine, offered by the Dynamical Theory of Gases.** By A. W. RÜCKER (*Phil. Mag.* [5], 9, 35—39).—The specific heats of a gas at constant volume ( $C_v$ ) and constant pressure ( $C_p$ ), and the degrees of freedom ( $m$ ) of the molecules of which it is composed are connected together by the equations

$$(1) (C_p - C_v)\delta = 0.694; (2) \frac{C_p}{C_v} = + \frac{2}{m + e}; \text{ where } e = \text{a quantity depending on the potential energy of the molecule.}$$

Kundt and Warburg find for mercury vapour  $\frac{C_p}{C_v} = 1.666$ , from which it would

follow that the atoms of mercury are smooth, rigid spheres. For O, N, H, CO, NO, and air,  $\frac{C_p}{C_v} = 1.4$ , which agrees with the supposition

that their molecules are surfaces of revolution, for which Boltzmann and Bosanquet have pointed out that  $m = 5$ ,  $e = 0$ . Such a surface of revolution would be formed by two spheres rigidly united, or, as is more probably the case, bound together by forces which prevent the separation of their surfaces, while leaving them otherwise free to move. The maximum number of degrees of freedom of a molecule composed of  $n$  smooth rigid spheres would be  $3n$ , but this value would generally be reduced by the forces acting between the spheres;  $m + e$  could not be greater, but might be less than  $3n + e$ . For a molecule composed of 2 atoms  $e = 0$ , but this value will probably increase with the complexity of the molecule. Two tables are given, the first showing the values of  $\frac{C_p}{C_v}$ ,  $m + e$ , and  $3n$  for Hg, O, N, H,

air, and several compounds of C, H, O, and S, and N; the second showing the values of the same quantities for certain compounds of chlorine. In the first table  $m + e$  is always less than  $3n$ , except in the case of Hg, when the two quantities are equal; in the second  $m + e$  is greater than  $3n$  for more than two-thirds of the compounds given. This difference may be explained by supposing either that in the case of chlorine  $e$  is abnormally large, which would agree with the supposition that the atoms composing the molecule are less firmly united; or that  $n$  has been taken too small, i.e., the molecule of chlorine consists of more than 2 atoms. In the last column of the second table are given the values of  $3n$  on the supposition that Cl<sub>2</sub> should be written for Cl. The differences between  $3n$  and  $m + e$  are now of the same order and sign as in Table I. Hydrochloric acid ( $m + e = 5$ ), however, presents a difficulty, since the degrees of freedom of a molecule composed of four spheres would be greater than five, unless the spheres were rigidly connected, with their centres in the same straight line. Bromine, and monohromethane, the only one of its compounds which has been studied, show similar differences. These observations have a special interest in connection with V. Meyer's researches on the vapour-density of chlorine. C. H. B.

**Relations between the Pressures, Temperatures, and Densities of Saturated Vapours.** By A. WINKELMANN (*Ann. Chem. Phys.*, [2], 9, 358—393).—This paper is a continuation of a previous

communication, and in it the author discusses mathematically the formulæ which have been proposed for expressing the relations between the pressure, temperature, and density of the vapours of ether, carbon bisulphide, carbon chloride, acetone, and chloroform. He gives tables in which the observed values in many series of experiments are compared with values calculated from the formulæ. R. R.

**Heat of Vaporisation of Sulphuric Anhydride.** By BERTHELOT (*Compt. rend.*, 90, 1510—1511).— $\text{SO}_3$  gas +  $\text{H}_2\text{O}$  + water =  $\text{SO}_4\text{H}_2$  dilute, evolves + 49.2 cal.; the hydration of solid  $\text{SO}_3$  (80 grams) evolves + 37.4 cal., hence the vaporisation of  $\text{SO}_3$  (80 grams) at about  $18^\circ$  absorbs - 11.8 cal., a number which does not differ greatly from that for the vaporisation of solid  $\text{H}_2\text{O}$  (18 grams) at  $0^\circ$ , 12.3 cal. C. H. B.

**Solubility of Solids in Gases.** By J. B. HANNAY and J. HOGARTH (*Chem. News*, 41, 103).—The term "gas" is applied to a fluid at any temperature above its critical point. Alcohol gas dissolves potassium iodide, &c., and no deposition of solid occurs at temperatures much above the critical point. The spectrum of cobaltous chloride dissolved in alcohol gas at  $320^\circ$  is identical with that of the chloride at  $15^\circ$ . The critical point of alcohol gas is  $234.6^\circ$ , at a pressure of 65 atmospheres; if the gas contain dissolved potassium iodide, the critical point is  $237^\circ$  for 71.1 atmospheres pressure.

A simple and efficient modification of Andrews's apparatus is described. M. M. P. M.

**"Flashing" in Assays of Gold.** By A. D. v. RIEMSDIJK (*Chem. News*, 41, 126).—When a mixture of gold, copper, and silver in certain proportions is cupelled with lead at a temperature above the melting point of gold, the liquid metal on leaving the muffle cools below redness, and then suddenly emits a clear greenish light.

Any means which prevents the complete fusion of the alloy of gold and silver, or disturbs the equilibrium of the cooling mass, prevents the phenomenon of "flashing." The phenomenon is explained by the author by supposing that the molten alloy is in a superfused state, and that as it cools a limit of temperature is reached at which it suddenly parts with its latent heat of fusion; this evolution of heat is attended with a flash of light.

The paper contains details of the circumstances which prevent flashing, and also deals with the practical application of the phenomenon in testing gold for metals of the platinum group, some of which do, whilst others do not prevent flashing, and in other departments of gold assaying. M. M. P. M.

**Chemical Repulsion.** By E. J. MILLS (*Chem. News*, 41, 40).—A glass plate is covered with barium chloride solution, and another plate, with a perforation at the centre, is pressed upon the first. When only a thin film of the solution remains between the plates, a little dilute sulphuric acid is introduced through the perforation. Barium sulphate is formed, and slowly spreads between the plates. If the upper



plate have two circular perforations, and if sulphuric acid be introduced at each, two circles of barium sulphate are formed, but the circles exercise a visible retardation on each other at their neighbouring edges.

If the perforations are equidistant from the centre of a square plate and situated on the diagonal of the plate, the other diagonal is eventually traced out in a line of no chemical action.

Various modifications of the experiment are described. The author concludes that "chemical action can take place at a distance," and that "two or more chemical actions, identical except in position, completely exclude one another." M. M. P. M.

**Molecular Volumes of Solid Carbon Compounds.** By H. SCHRODER (*Ber.*, 13, 1070—1076).—This is a continuation of the author's previous papers (*ibid.*, 12, 561, 1612; this Journal, Absts. (1879), 610; (1880), 21.

|  | Molec. wt. | Sp. gr.  | Molec. vol. |
|--|------------|----------|-------------|
| Carbon sesquichloride, $C_2Cl_6$ .....                               | 237.0      | 2.011    | 117.8       |
| Phthalic acid, $C_8H_6O_4$ .....                                     | 166.0      | 1.593    | 104.2       |
|  |            | 1.585    | 104.8       |
| Quinone, $C_6H_4O_2$ .....   | 108.0      | 1.307    | 82.6        |
|  |            | 1.318    | 81.9        |
| Anthraquinone, $C_{14}H_8O_2$ .....                                  | 208.0      | 1.438 to | 144.7 to    |
|  |            | 1.419    | 146.6       |
| Phenanthraquinone, $C_{14}H_8O_2$ .....                              | 208.0      | 1.404    | 148.2       |
|  |            | 1.405    | 148.1       |
| Metanitrochlorbenzene, $C_6H_4NO_2Cl$                                | 157.5      | 1.534    | 102.6       |
| Thiocarbamide, $CSN_2H_4$ .....                                      | 76.0       | 1.406    | 54.1        |
|  |            | 1.450    | 52.4        |
| Diethylcarbamide, $C_5H_{12}N_2O$ .....                              | 116.0      | 1.040    | 111.6       |
|  |            | 1.043    | 111.3       |
| Guanidine carbonate, $C_3H_{12}N_6O_3$ ..                            | 180.0      | 1.251    | 143.9       |
|  |            | 1.238    | 145.4       |
| Styracin, $C_{18}H_{16}O_2$ , m. p. 40—41° }<br>(= 44°, Muller)..... | 264.0      | 1.154    | 228.8       |
|  |            | 1.159    | 227.8       |
| Citraconic acid, $C_8H_6O_4$ .....                                   | 130.0      | 1.618    | 80.4        |
|  |            | 1.616    | 80.5        |
| Itaconic acid, $C_6H_4O_4$ .....                                     | 130.0      | 1.632    | 79.7        |
|  |            | 1.573    | 82.6        |
| Pyrotartaric acid, $C_6H_6O_4$ .....                                 | 132.0      | 1.413    | 93.4        |
|  |            | 1.408    | 93.8        |
| Uric acid, $C_5H_4N_4O_3$ .....                                      | 168.0      | 1.855    | 90.6        |
|  |            | 1.893    | 88.8        |
| Cyanuric acid, $H_3C_3N_3O_3 + 2Aq$ ..                               | 165.0      | 1.722    | 95.8        |
|  |            | 1.735    | 95.1        |
| Camphoric acid, $C_{16}H_{16}O_4$ , m. p. = }<br>177—178°.....       | 200.0      | 1.195    | 167.5       |
|  |            | 1.191    | 168.0       |
| Monobromcamphor, $C_{10}H_{15}BrO$ , m. p. }<br>= 76° .....          | 231.0      | 1.437    | 160.8       |
|  |            | 1.449    | 159.4       |
| Benzoic acid, $C_7H_6O_2$ .....                                      | 122.0      | 1.288 to | 94.7 to     |
|  |            | 1.314    | 92.8        |

|  | Molec. wt. | Sp. gr.  | Molec. vol.    |
|--|------------|----------|----------------|
| Sodium nitroprusside,<br>$\text{Na}_2\text{FeC}_5\text{N}_6\text{H}_4\text{O}_3$ ..... | 298.0      | 1.713    | 173.5          |
|  |            | 1.731    | 172.1          |
|  |            | 1.687    | 176.7 (Dudley) |
| Mercuric cyanide, $\text{HgCy}_2$ .....  | 252.0      | 3.990    | 63.2           |
|  |            | 4.011    | 62.8           |
| Silver cyanide, $\text{AgCy}$ .....  | 134.0      | 3.988    | 33.6           |
| Pyrocatechnic acid, $\text{C}_7\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O}$ ..       | 172.0      | 1.542 to | 111.6 to       |
|  |            | 1.541    | 111.7          |
| Gallic acid, $\text{C}_7\text{H}_6\text{O}_5 \cdot \text{H}_2\text{O}$ .....           | 188.0      | 1.703    | 110.4          |
|  |            | 1.685    | 111.5          |
| Morphine, $\text{C}_{17}\text{H}_{19}\text{NO}_3 \cdot \text{H}_2\text{O}$ .....       | 303.0      | 1.326    | 228.5          |
|  |            | 1.317    | 230.1          |
| Codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3 \cdot \text{H}_2\text{O}$ .....        | 317.0      | 1.323    | 239.6          |
|  |            | 1.311    | 241.8          |
| Thebaine, $\text{C}_{19}\text{H}_{21}\text{NO}_3$ .....                                | 311.0      | 1.305    | 238.3          |
|  |            | 1.282    | 242.6          |
| Laudanine, $\text{C}_{20}\text{H}_{25}\text{NO}_4$ .....                               | 348.0      | 1.256    | 273.1          |
|  |            | 1.255    | 273.3          |
| Cryptopine, $\text{C}_{21}\text{H}_{23}\text{NO}_5$ .....                              | 369.0      | 1.351    | 273.1          |
| Papaverine, $\text{C}_{21}\text{H}_{21}\text{NO}_4$ .....                              | 351.0      | 1.337 to | 262.5 to       |
|  |            | 1.308    | 268.4          |
| Narcotine, $\text{C}_{22}\text{H}_{22}\text{NO}_7$ .....                               | 413.0      | 1.374 to | 300.6 to       |
|  |            | 1.395    | 296.1          |

Cases are mentioned confirming the former statement that carbon, hydrogen, and oxygen always occupy the space of one stere.

T. C.

## Inorganic Chemistry.

**Density of Iodine Vapour.** By L. TROOST (*Compt. rend.*, 91, 54—56).—The iodine was volatilised in porcelain globes of 250—300 c.c. capacity, glazed inside and out, which were placed in a muffle and heated in an oil furnace, the temperatures being determined by means of the air thermometer previously described. Assuming that the coefficient of expansion of iodine vapour is the same as that of air, the following results were obtained :—

|                |         |       |       |
|----------------|---------|-------|-------|
| Temperature .. | 1235.5° | 1241° | 1250° |
| Density .....  | 5.82    | 5.71  | 5.65  |

The density was also determined at the boiling point of sulphur under varying pressures, assuming that iodine vapour obeys Boyle's law :—

|              |           |      |      |       |       |
|--------------|-----------|------|------|-------|-------|
| Pressure.... | 768.0 mm. | 67.2 | 48.6 | 48.57 | 34.52 |
| Density .... | 8.70      | 8.20 | 7.75 | 7.76  | 7.35  |

The author considers that these results indicate, not dissociation or

an isomeric change, but that the coefficients of expansion and compressibility of iodine vapour vary respectively with the temperature and pressure. C. H. B.

**Density of Iodine Vapour.** By V. MEYER (*Ber.*, 13, 1103—1116).—This is a reply to the remarks of Crafts and Meier (*Ber.*, 13, 851; this vol.), on the author's method (1) of determining the temperature, and (2) of taking vapour-densities. In regard to the former it is allowed that Crafts and Meier's objections are well founded, for, since the measurement of the temperature of the furnace is taken at a time very different from that at which the actual vapour-density determination is made, it is impossible to ensure that the temperature of the furnace remains constant throughout that length of time, and consequently the results obtained in this way do not give the correct relation between the temperature and the density. The author is at present engaged in experiments with a view to overcome this objection.

With respect to the objections as to the *modus operandi* in taking vapour-densities, it is shown by a number of special experiments that they are entirely without foundation, and that therefore the method formerly described gives correct results. T. C.

**Dissociation of Iodine Vapour.** By A. NAUMANN (*Ber.*, 13, 1050—1052).—On the assumption that the molecule  $I_2$  splits up into two atoms ( $I + I$ ), the author has constructed a table showing the amount of dissociation which iodine undergoes as the temperature increases. For this purpose the experimental numbers of Meier and Crafts (*ibid.*, 13, 851) are employed, and use is made of the formula  $p = \frac{100(d - D)}{(a - 1)D}$  (*Annalen*, 1867, Suppl., 5, 345), in which  $d$  = the normal density of the undecomposed gas,  $D$  the observed density,  $a$  the number of atoms into which the molecule is decomposed, and  $p$  the percentage amount of decomposition. Since  $a = 2$ , and  $d = \frac{2 \times 126.8}{28.943} = 8.76$ , the above becomes  $p = \frac{100(8.76 - D)}{D}$ .

The table so constructed shows that the course of the dissociation of iodine vapour is quite in accordance with the result required by the mechanical theory of gases, viz., that the increments of decomposition corresponding to equal differences of temperature increase gradually from the temperature at which dissociation commences, up to that at which 50 per cent. of the vapour is decomposed, and then decrease in a similar manner up to that temperature at which dissociation is complete.

Attention is drawn to the unusually large range of the temperature of dissociation, viz., from about 600° to about 1800°. T. C.

**Physical Constants of Hydrochloric Acid.** By G. ANSDALL (*Chem. News*, 41, 75).—The gas was condensed in a Cailletet pump.

| Temperature. | Density. | Temperature. | Coefficient of compression. |
|--------------|----------|--------------|-----------------------------|
| 0°           | 0·908    | 47·0°        | 0·00166                     |
| 7·5          | 0·873    | 41·6         | 0·00123                     |
| 11·67        | 0·854    | 33·0         | 0·00096                     |
| 15·85        | 0·835    | 22·9         | 0·000635                    |
| 22·7         | 0·808    | 15·85        | 0·00062                     |
| 33·0         | 0·748    | 10·5         | 0·00054                     |
| 41·6         | 0·678    | 5·7          | 0·000397                    |
| 47·8         | 0·619    | —            | —                           |

| Temp. | Vol. of saturated vapour at point of liquefaction. | Fractional vol. of gas at point of liquefaction referred to initial vol. under one atmosphere. | Volume of condensed liquid. | Ratio of vol. of liquid to that of gas. | Pressure in atmospheres. |
|-------|--|--|-----------------------------|---|--------------------------|
| 0·00° |  |  |                             |   |                          |
| 4·00  | 137·31   | $\frac{1}{38·89}$  | 7·35                        | 18·18                                   | 29·8                     |
| 9·25  | 118·96   | $\frac{1}{45·75}$  | 7·90                        | 15·05                                   | 33·9                     |
| 13·8  | 103·60   | $\frac{1}{53·19}$  | 8·35                        | 12·39                                   | 37·75                    |
| 18·1  | 91·77  | $\frac{1}{61·17}$  | 8·74                        | 10·50                                   | 41·80                    |
| 22·0  | 81·19  | $\frac{1}{70·08}$  | 9·10                        | 8·72                                    | 45·75                    |
| 26·75 | 69·69  | $\frac{1}{82·94}$  | 9·50                        | 7·33                                    | 51·00                    |
| 33·4  | 55·75  | $\frac{1}{105·98}$   | 10·12                       | 5·50                                    | 58·85                    |
| 39·4  | 44·85  | $\frac{1}{134·33}$   | 10·68                       | 4·19                                    | 66·95                    |
| 44·8  | 36·34  | $\frac{1}{168·67}$   | 11·96                       | 3·03                                    | 75·20                    |
| 48·0  | 31·33  | $\frac{1}{197·60}$   | 12·00                       | 2·61                                    | 80·80                    |
| 49·4  | 27·64  | $\frac{1}{224·96}$   | 12·92                       | 2·13                                    | 84·75                    |
| 50·56 | 25·70  | —  | 14·30                       | 1·79                                    | 85·53                    |
| 51·00 | 23·96  | —  | —                           | —                                       | —                        |

M. M. P. M.

**Analyses of Air.** By H. MACAGNO (*Chem. News*, 41, 97).—The analyses are of the air of Palermo. A marked deficiency of oxygen is shown during the prevalence of the *sirocco* wind (March 20th, 19·994, and May 31st, 20·017 per cent. by volume).

The mean results are as follows:—

*February to May.*

Gram per 100 litres.

| O (volume). | CO <sub>2</sub> . | HNO <sub>3</sub> . | NH <sub>3</sub> . | Organic matter. | Mean temperature. | Rainfall in mm. |
|-------------|-------------------|--------------------|-------------------|-----------------|-------------------|-----------------|
| 20.717      | 0.033             | 0.000              | 0.008             | 0.102           | 14.2°             | 173.18          |

*June to August.*

|        |       |        |       |       |      |      |
|--------|-------|--------|-------|-------|------|------|
| 20.920 | 0.039 | traces | 0.009 | 0.160 | 23.4 | 0.00 |
|--------|-------|--------|-------|-------|------|------|

M. M. P. M.

**Variations in the Composition of the Atmosphere.** By P. v. JOLLY and E. W. MORLEY (*Bied. Centr.*, 1880, 230—231).—The first-named author employs two methods for the estimation of atmospheric oxygen and nitrogen; the results of both fully correspond. First, the weighing of a definite volume of air in conjunction with the estimation of the sp. gr. of oxygen and nitrogen, and afterwards the direct eudiometric analysis of the air; the direction of the wind currents too must be closely observed. The end result of the observations shows that the oxygen of the atmosphere is subject to not inconsiderable variations. In the year 1877 the amount of oxygen varied from 21.01 to 20.53 per cent. in the years 1875–76, 20.96—20.47 per cent.; in both years the highest figures were obtained during north, and the lowest during the prevalence of southerly winds, but it is not affirmed that these directions of the air currents are always accompanied by or are a cause of these phenomena. A change of wind, however, from one to other of these directions is generally followed by a variation of a half of a per cent. in the composition of the air, and a brisk rapidly changing wind is the best condition for obtaining well mixed air. Further observations are looked forward to to show that notwithstanding the richer vegetation of the tropics, the process of oxidation is more active there than that of reduction, whilst the reverse is taking place in northern regions.

Morley, in the *American Jour. Science*, takes the foregoing experiments into consideration, and says that if Jolly's results are trustworthy, and show, by an examination of the air of the temperate zone, such differences, after travelling thousands of miles and being blended with the air of the intermediate countries, the actual difference when estimated near the pole and the equator must be great indeed, and greater than there is any reason for supposing. He therefore thinks further research necessary. According to a theory recently propounded by Loomis, the sudden lowerings of temperature are not caused by the passage of cold currents of air from higher to lower latitudes, but rather by the vertical descent of masses of cold air from the upper regions of the atmosphere to the lower. Morley says if this be the case, it is easy to understand that during the lowering of the temperature the air in the vicinity of the earth's surface should contain less than the average amount of oxygen, and that a sample of air taken from such a descending mass is in reality a sample of the upper stratum of the atmosphere before mixing with the underlying strata, and it is also possible that if that sample was part of a mass which had long been in the higher regions, it might have lost some of the oxygen

which it contained when resting on the surface of the ocean. He also directs attention to the fact that Jolly's analyses showed the following quantities of oxygen:—20·48—20·50, 20·49—20·46, 20·56, and that in Fehling's "*Neues Handwörterbuch der Chemie*," an analysis of air from the Bay of Bengal gives oxygen at 20·46, one from the neighbourhood of Calcutta, 20·39, and from the vicinity of Algiers, 20·41. So that from this it is improbable that such great differences really exist.

J. F.

### Variations in the Carbonic Anhydride of the Atmosphere.

By P. HASSELBARTH and J. FITTBOGEN (*Bied. Centr.*, 1880, 161—164).

—The experiments recorded in this paper were undertaken in consequence of the considerable differences existing between the observations of Saussure and Boussingault on the one hand, and Schulze (at Rostock) on the other; they were also intended to throw light on the effect of local influences on such variations.

The following is the record of experiments:—

The average of 347 estimations made at the station of Dahme show a mean of 3·24 vols. of carbonic anhydride in 10,000 of air, which serves to confirm the assertion of Schulze that Saussure and Boussingault's estimate of 4 to 4·15 was too high. Henneberg in estimations made at Weende found an average of 3·2 per cent., which is confirmatory of those of the author. Both localities are about the same distance from the sea.

At Rostock 1,600 estimations were made, the mean of which was only 2·92 vols. in 10,000 of atmospheric air; the difference appears to be caused by the situation of the place close to the sea, the water of which possesses such power of absorption for carbonic anhydride. At Dahme the figures varied monthly, and were lowest in December, which the authors ascribe to the cold retarding the ordinary processes of decay.

The figures also show an intimate connection with the direction and strength of the wind, its direction having most influence. In Dahme the *west wind* always caused an increase; at Rostock there was an increase during *northerly* winds, and a diminution during south-westerly. An increase in the force of the wind, no matter from what direction, invariably decreases the amount of carbonic anhydride, and after high winds or storms, it almost always increases; when this does not occur, it is due to maintenance of higher winds than usual or a change in their direction.

Rain generally causes a depression; a thaw causes a decrease, fog sometimes a small increase, sometimes a decrease.

A course of experiments made during the summers of 1876—1877 in Dahme on evaporation from plants shows a general decrease in carbonic anhydride from sunrise to mid-day, from thence to sunset a regular increase. All experiments show a sudden decrease shortly after sunrise, which is attributed to the action of the awakened and refreshed plants.

J. F.

**Formation of Hydrogen Peroxide and Ozone by the Action of Moist Phosphorus on Air.** By A. R. LEEDS (*Ber.*, 13, 1066—1070).

—The former statement (*Annalen*, 200, 286) that both hydrogen peroxide and ozone are produced by the action of moist phosphorus on air, is confirmed. The dilute solution of these two bodies is not completely decomposed even after long standing. When the current of ozonised air is passed through a tube heated to different temperatures, the amount of water produced by the decomposition of the hydrogen peroxide increases with the temperature, whilst the quantity of ozone regularly diminishes up to 200°, when it disappears altogether; if after this point is reached, the aqueous solution of the gases is titrated with a slightly acid (sulphuric) instead of a neutral solution of potassium iodide, the latter undergoes slow decomposition, which is not due to ozone, but to the action of ordinary oxygen. T. C.

**An Experiment with Sulphur.** By T. GROSS (*Chem. Centr.*, 1879, 785).—The author doubts the elementary character of sulphur. By heating a mixture of sulphur (commercial milk of sulphur)\* and linseed oil in an open basin, he obtained a black porous mass, which dissolved in concentrated sulphuric acid, after long-continued heating, to form a syrupy liquid. After dilution, sulphuretted hydrogen was passed into this liquid, and produced a light brown precipitate, soluble in ammonium sulphide or in hot potash solution. When burnt in air, this precipitate left a black residue, which was not acted on by inorganic acids, was not attacked by oxygen even at a red heat, and was but slowly and partially changed by chlorine with formation of a sublimate, which was reduced to the original black substance by the action of hydrogen. M. M. P. M.

**Crystallised Calcium Oxide.** By A. LEVALLOIS and S. MEUNIER (*Compt. rend.*, 90, 1566—1568).—A crystalline mass, in some parts white, in others slightly coloured, found on the lining of a continuous lime-kiln which had been in almost uninterrupted operation at Champigny for 28 months, consisted partly of rounded grains, partly of small distinct cubical crystals. These crystals, the angles of which were in some cases slightly modified, were opalescent and had no action on polarised light. When exposed to the air they slowly absorbed a small quantity of water and carbonic anhydride, and when placed in water were gradually dissolved. Dilute acids were almost without action in the cold, but, if slightly warmed, the crystals were rapidly dissolved with considerable evolution of heat, but no gas was given off. Analysis gave the numbers  $\text{CaO}$ , 96.9;  $\text{H}_2\text{O}$ , 1.9; insoluble matter, 0.8 = 99.6; sp. gr., 3.32. Probably the crystalline oxides of the allied metals and magnesium may be formed in a similar way.

C. H. B.

*Note.*—Brügelmann (this Journal, 1878, Absts. 471 and 771) has obtained crystals of lime, baryta, and strontia by strongly heating the nitrates in covered crucibles.—C. H. B.

**Reactions between Calcium Carbonate and Ammoniacal Salts.** By NIVER (*Compt. rend.*, 90, 1216—1218).—Calcium car-

\* The attempt seems to have been made by the author to ascertain whether the sulphur was pure or not.

bonate when boiled with solutions of ammoniacal compounds or nitrogenous organic bodies, causes the evolution of ammonia equally as well as magnesia. With solutions of ammonium salts, the evolution of ammonia, probably as carbonate, takes place even at ordinary temperatures. The ammonia naturally present in soils is probably mainly in the form of carbonate; that added as manure is generally in the form of sulphate. A calcareous soil very rich in humus, a very clayey soil, a sandy soil, and Fontainebleau sand, when mixed with water, ammonium chloride, and calcium carbonate, evolved respectively in 23 days at a mean temperature of  $23^{\circ}$ , 0.00303 gram, 0.00310 gram, 0.01390 gram, and 0.02120 gram of ammonia. The volatilisation of ammonia is also effected by passing a current of air, free from carbonic anhydride, through solutions of various ammonium salts, in the presence of calcium carbonate. If, however, the air be replaced by carbonic anhydride only, a mere trace of ammonia is given off. Soils rich in organic matter also contain considerable quantities of carbonic anhydride, which will tend, therefore, to prevent the diffusion of the ammonia into the atmosphere. It would appear, then, that in waters and in soils a double decomposition takes place between ammoniacal salts and calcium carbonate, tending to cause a loss of ammonia, which in the case of a soil will be greater the greater its absorbent properties, and less the greater the amount of carbonic anhydride in the gases in the soil.

C. H. B.

**Characteristics of the Alkaline Earths and of Zinc Oxide.** By G. BRÜGELMANN (*Zeits. Anal. Chem.*, 1880, 283—290).—Calcium oxide is obtained in the amorphous condition by ignition of the hydrate or carbonate, whilst from the nitrate it is obtained in cubes; the sp. gr. of both forms is 3.25.

Strontium oxide, from the oxide or carbonate, is amorphous and of sp. gr. 4.51, that from the nitrate crystallises in cubes, and has a sp. gr. of 4.75. Barium oxide prepared from the hydrate forms microscopic needles, which cannot belong to the regular system, as they show chromatic polarisation; the sp. gr. is 5.32; the nitrate on ignition yields microscopic cubes of sp. gr. 5.78. Magnesium oxide was invariably obtained amorphous, and of sp. gr. 3.42. Zinc oxide from the carbonate or hydrate is amorphous; sp. gr. 5.47; that from the nitrate forms microscopic hexagonal pyramids of sp. gr. 5.78.

A. J. G.

**Revision of the Atomic Weights and Quantivalence of Aluminium.** By J. W. MALLETT (*Chem. News*, 41, 212—213).—In the determination of the atomic weight, vessels of platinum or hard porcelain were used where possible instead of glass.

In the first series of experiments the aluminium oxide was determined, which resulted from the ignition of a known weight of ammonium alum.

In the second series a solution of aluminium bromide was precipitated by silver nitrate, and the ratio was obtained of the silver used to form the silver nitrate, to the aluminium bromide.

In the third series, pure aluminium (obtained by the reduction of the bromide by sodium) was dissolved in a solution of pure soda, and the



hydrogen evolved was either measured directly or burnt to water, and weighed as such.

In the following epitome of the results, A, B, C denote groups of experiments under each series, the experiments of each group differing only in the quantity of material operated on, while the different groups differ in the different preparation used, or in some feature of the method. Thus in Series I, A was made with alum, dried by exposure to air for two hours; B with alum dried by exposure for twenty-four hours. In Series II, A, B, C were made with successive portions of a distillate of aluminium bromide. In Series III, A was made by estimating the hydrogen by volume, B by weighing the water formed by its combustion. Only the number of experiments in each group, the mean results from the group, and the probable error of the mean are here given:—

*Series I.*

|                    | A.              | B.               | C. |
|--------------------|-----------------|------------------|----|
| Number .....       | 5               | 5                | —  |
| Mean .....         | 27·040          | 27·096           | —  |
| Probable error.... | $\pm 0\cdot073$ | $\pm 0\cdot0054$ | —  |

*Series II.*

|                    | A.               | B.               | C.               |
|--------------------|------------------|------------------|------------------|
| Number .....       | 3                | 5                | 3                |
| Mean .....         | 27·034           | 27·023           | 27·018           |
| Probable error.... | $\pm 0\cdot0049$ | $\pm 0\cdot0052$ | $\pm 0\cdot0069$ |

*Series III.*

|                    | A.               | B.               | C. |
|--------------------|------------------|------------------|----|
| Number .....       | 6                | 3                | —  |
| Mean .....         | 27·005           | 26·990           | —  |
| Probable error.... | $\pm 0\cdot0033$ | $\pm 0\cdot0046$ | —  |

From the fact that crystallised ammonium alum gradually loses water on exposure to air, least confidence is reposed in Series I, B, most weight being attached to Series III, A, the resulting hydrogen occupying a large volume, and direct comparison being made with it, without the intervention of other atomic weights. The mean from the thirty experiments, all included, is  $Al = 27\cdot032$ , with a probable error of  $\pm 0\cdot0045$ . Excluding Series I, B, the mean of the remaining twenty-five is  $Al = 27\cdot019$ , with a probable error of  $\pm 0\cdot0030$ .

F. L. T.

**Edible Earth from Japan.** By E. G. LOVE (*Chem. News*, 41, 187—188).—The analysis of a specimen of this earth, from Toietonai (Eat-Earth Valley), on the north coast of Yesso, and used by the Ainos as food, gave the following results:—

|                           |             |       |
|---------------------------|-------------|-------|
| Silicon                   | oxide ..... | 67.19 |
| Aluminium                 | „ .....     | 13.61 |
| Iron                      | .....       | 1.11  |
| Manganese                 | .....       | 0.07  |
| Calcium                   | .....       | 3.89  |
| Magnesium                 | .....       | 1.99  |
| Potassium                 | .....       | 0.23  |
| Sodium                    | .....       | 0.75  |
| Sulphuric anhydride       | .....       | 0.19  |
| Phosphoric                | „ .....     | trace |
| Water and volatile matter | .....       | 11.02 |

100.05

It is of a light grey colour, and very fine in structure. This analysis shows that the earth is essentially an aluminium silicate with silicon anhydride, and is similar in composition to those eaten by the Javanese and Laplanders. This clay is eaten as soup, being boiled with lily roots in a small quantity of water, and afterwards strained.

F. L. T.

**Retrogradation of Superphosphates containing Iron and Aluminium.** By C. F. MEYER (*Zeits. Anal. Chem.*, 1880, 309—311).—The previous conclusions of the author (*ibid.*, 1880, 145) are incorrect. Ferric sulphate acting on monocalcium phosphate yields gypsum and an acid ferric phosphate, which in its turn acting on any tricalcic phosphate present, forms insoluble ferric phosphate together with equal quantities of mono- and di-calcic phosphates.

A. J. G.

**Atomic Weight and Characteristic Salts of Ytterbium.** By L. F. NILSON (*Compt. rend.*, 91, 56—59).—About 20 grams of pure ytterbia were isolated from 6 kilos. of the crude earths obtained from many kilos. of gadolinite and euxenite by the method already described. The oxide was dissolved in acid, the solution treated with hydrogen sulphide, and the ytterbium precipitated as oxalate, which when heated gave the oxide in a perfectly pure condition. The mean of seven concordant determinations of the atomic weight by converting the oxide into the anhydrous sulphate was 173.01.

The oxide,  $\text{Yb}_2\text{O}_3$ , is a white infusible powder, sp. gr. 9.175, insoluble in water, easily soluble in hot dilute acids, but attacked with difficulty, even by strong acids, in the cold. Its solutions have a sweet astringent taste, are colourless, and give no absorption-spectrum. The salts impart no colour to the Bunsen flame, but with the electric spark the chloride gives a brilliant spectrum. The nitrate forms large crystals, which melt in their water of crystallisation at  $100^\circ$ , and decompose when heated with evolution of nitric acid and nitrous fumes, and formation of insoluble basic nitrates. The sulphate,  $\text{Yb}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ , forms large brilliant prisms which do not alter when exposed to the air, but lose their water at  $100^\circ$ . It dissolves slowly in boiling water, and is completely soluble in a saturated solution of potassium sulphate. The anhydrous sulphate may be heated to a high temperature without decomposition, but at a white heat is com-

pletely converted into oxide. The normal selenite is obtained as a voluminous amorphous precipitate by mixing solutions of sodium selenite and ytterbium sulphate. When treated with excess of selenious acid it yields an insoluble crystalline acid selenite,  $\text{Yb}_2\text{SeO}_3 \cdot \text{H}_2\text{SeO}_3 \cdot 4\text{H}_2\text{O}$ , which loses its water at  $100^\circ$ . The oxalate,  $\text{Yb}_2\text{C}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ , is formed as a voluminous precipitate of small fine needles by the addition of oxalic acid to a solution of an ytterbium salt; this precipitate soon contracts, and assumes the form of short thick prisms. It loses  $7\text{H}_2\text{O}$  at  $100^\circ$ , and is but slightly soluble in water and dilute acids.

That ytterbia is a sesquioxide is shown by the composition of the sulphate, analogous to and isomorphous with those of yttrium and didymium; by the composition of the acid selenite, and by that of the oxalate and formate, analogous respectively to the corresponding salts of didymium and yttrium; and, lastly, by the molecular heats and volumes of the oxide and the anhydrous sulphate. C. H. B.

**Action of Potassium Chlorate on Ferrous Iodide.** By R. H. PARKER (*Pharm. J. Trans.* [3], 10, 850—851).—By mixing syrup of iodide of iron and potassium chlorate together, and allowing the mixture to stand, iodine separates out, and a red precipitate is formed, which appears to be ferric oxide with 1 mol. of water,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The reaction is accelerated by heating the mixture, and also by adding excess of potassium chlorate. During the gradual precipitation in the cold the iron remaining in solution exists in the ferrous state, but when the action is complete the whole of the iron is precipitated. The reaction may be expressed  $2\text{FeI}_2 + \text{KClO}_3 + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{I}_2 + \text{KCl}$ ; it is not quite certain what amount of potassium chloride is formed, but the question is being investigated. L. T. O'S.

**Composition and Analysis of Weldon Mud.** By H. LUNGE (*Chem. News*, 41, 129 and 141).—This paper is mainly devoted to a criticism of a communication by Post in the *Berichte* (12, 1454). The author details experiments which prove that the results obtained by acting on the "mud" with ferrous sulphate, and titrating residual iron by permanganate, are identical with those obtained by Bunsen's iodometric method.

For estimating total manganese he gives the preference to Weldon's original method of boiling with bleaching powder, with subsequent titration of the precipitate by iron and permanganate; he shows that the "mud" may be boiled directly with bleaching powder without previous solution in acid.

His experiments also confirm Weldon's view of the composition of the "mud," so far as the existence of a "base" is concerned.

M. M. P. M.

**Atomic Weight of Antimony.** By J. P. COOKE (*Chem. News*, 41, 201—203).—In a previous paper (*Proc. Am. Ac. Art. Sci.*, 2, 11) reasons were given for preferring antimonious bromide as the body for determining the atomic weight of antimony from, and 15 results were given, with the mean value 120.00 varying between 119.4 and 120.4. These previous results were obtained from the gravimetric-

determination by silver in presence of tartaric acid, of the bromine in antimonious bromide, purified by fractional distillation and crystallisation from carbon bisulphide. An apparatus was also described for subliming antimonious iodide. This has been applied to the sublimation of the bromide with excellent results.

The process now adopted is a volumetric one. If the atomic weight of antimony were 122.00 it would require 1.79 grams of pure silver to 2.0 grams of the bromide; if it were 120.00 it would require 1.80 grams of silver to the same amount of bromide.

Varying weights (2—4 grams) of the bromide prepared by sublimation were taken, and slightly less than the corresponding amounts of pure silver were dissolved in nitric acid, evaporated to dryness, and added to the tartaric acid solutions of the bromide. The excess of silver required being run in from a burette, and measured with the usual precautions. No indicator was used.

Five results obtained by this method are given, with the mean value 120.01, and varying from 119.98 to 120.02. The atomic weights of silver and bromine being taken as 108 and 80 respectively.

To check the work in two of the determinations the silver bromide was collected, washed, and weighed, first after drying at 150° C., and secondly after incipient fusion. The loss was one-tenth and two-tenths of a milligram at the second weighing in the two cases.

These two determinations give the amount of bromine present from the silver bromide found, and the corresponding values of Sb were 120.00 and 120.01.

F. L. T.

**Volatilising Point of Metallic Arsenic.** By G. M. CONECHY (*Chem. News*, 41, 189).—On heating together metallic arsenic (in an atmosphere of hydrogen), argentic chloride, argentic phosphate, and zinc iodide, gradually until the arsenic had yielded a distinct sublimate, it was found that the zinc iodide, m. p. 446° (Carnelley), had completely melted, and the argentic chloride, m. p. 457° (Carnelley) had agglomerated, and was on the point of melting. From this 449—450° is considered to be the volatilising point, although different authors give temperatures varying from 180° to a dull red heat.

F. L. T.

**Preparation of Potassium-bismuth Iodide.** By J. C. THRESH (*Pharm. J. Trans.* [3], 10, 641).—A solution of potassium bismuth iodide may be readily prepared by mixing 1.5 parts potassium iodide and 8 parts liq. bismuthi (B. P.) with 1.5 parts hydrochloric acid. This solution forms a very delicate reagent for the alkaloids, producing an orange-red precipitate. 1 part of strychnine in 500,000 parts of water and 1 part of morphine in 20,000 parts of water, may be detected by this means.

L. T. O'S.

**Reduction of Gold Chloride by Hydrogen in presence of Platinum.** By D. TOMMASI (*Chem. News*, 41, 116).—Gold chloride is not reduced to metallic gold by the action of hydrogen alone, nor by the action of platinum alone; but it is reduced by hydrogen in presence of platinum. The author thinks that hydrogen being absorbed by the platinum disengages heat, and that this disengagement of heat

determines a reaction between the hydrogen and gold chloride. One of the results (not, as supposed by Phipson, the cause) of this action is the production of an electric current. M. M. P. M.

**Action of Sulphuric Acid on Platinum.** By SCHEURER-KESTNER (*Compt. rend.*, 91, 59—62).—The action of chamber vitriol on the platinum retorts used in the process of concentration is due to the presence of a very minute trace of oxides of nitrogen, which gives scarcely any reaction with ferrous sulphate, but may be detected by means of the blue colour formed by diphenylamine. The solvent action is greater the greater the concentration of the acid. The oxides of nitrogen exist in the oil of vitriol in presence of selenium and sulphurous anhydride, and are apparently in a state of stable combination, since they are not expelled during the process of concentration, whereas all the sulphurous anhydride is given off. A very minute trace of nitrogen oxides, which appear to act as intermediate agents in the oxidation of the platinum at the expense of the oxygen of the sulphuric acid, is consequently sufficient to cause continuous solution of the platinum so long as the oil of vitriol remains in contact with it. If, however, the oil of vitriol be previously boiled with a little ammonium sulphate, all the oxides of nitrogen are destroyed, and the action on the platinum is prevented. Perfectly pure sulphuric acid does not attack platinum even when heated with it in closed tubes at the boiling point of sulphur. C. H. B.

**Compound Platinates and a New Platino-potassium Salt.** By L. PITKIN (*Chem. News*, 41, 118).—If platinic chloride and potassium bromide solutions containing these salts in the proportion of  $\text{PtCl}_4$  to  $2\text{KBr}$  are boiled together for some time, the salt  $2\text{KBr}.\text{PtCl}_4$  is formed; but if a considerable excess of potassium bromide is used, even in presence of hydrochloric acid, or if the salt  $2\text{KCl}.\text{PtCl}_4$  is boiled with potassium bromide solution, the double bromide  $2\text{KBr}.\text{PtBr}_4$  is produced. M. M. P. M.

**Action of Acids on Alloys of Rhodium with Lead and Zinc.** By H. DEBRAY (*Compt. rend.*, 90, 1195—1199).—When 1 part of rhodium is fused with 2—3 parts of lead in a carbon crucible the two metals combine, with evolution of light and heat, to form a crystalline alloy having the colour of bismuth. Dilute nitric acid removes the excess of lead, and leaves a residue composed partly of small, brilliant crystals of a definite alloy,  $\text{Pb.Rh}_2$ , insoluble in aqua regia, and partly of a blackish powder lighter than the alloy, from which it may be separated by levigation. The quantity of this powder formed is greater, the larger the quantity of lead in the original alloy. When the amount of lead exceeds 85 per cent. it constitutes the whole of the residue, in the form of blackish friable needles, without metallic lustre. Examined under the microscope the surfaces of the crystals are found to be rough, and corroded by the acid in which they have been formed. The alloy dissolves readily in aqua regia, and also in hot concentrated sulphuric acid with evolution of much sulphurous anhydride. On heating it, a small quantity of water is at first

given off, but at about  $400^{\circ}$  the substance decomposes with deflagration, evolving nitrogen and oxides of nitrogen, and leaving a residue of partially oxidised lead and rhodium. The composition of the substance varies with the amount of rhodium in the original alloy, and the duration of the action of the acid. Analyses gave Rh 63—66, Pb 15—20, hygroscopic moisture 2—3, O + N 15—17 per cent. The oxygen and nitrogen are in the proportion necessary to form nitric acid. It cannot be regarded as a basic nitrate of rhodium and lead, since the amount of oxygen is too small, and, moreover, potassium hydrate is without action on it; it is unlikely that it is analogous to nitrated organic compounds.

The residues left when alloys of zinc with iridium, ruthenium, and rhodium respectively are treated with concentrated hydrochloric acid, have no metallic lustre, and are readily soluble in aqua regia. When heated to about  $400^{\circ}$  they deflagrate violently without any appreciable evolution of gas, and the products of the deflagration have a metallic appearance, and are almost insoluble in aqua regia. It would appear that these alloys can exist in two isomeric modifications, one of higher energy than, and readily convertible into, the other. Nitric acid dissolves these residues with difficulty, but a considerable quantity of the acid combines with the residue, owing probably to capillary affinity. The resulting compounds, which can also be obtained by the direct action of nitric acid on the original alloys, explode at about  $400^{\circ}$ , evolving nitrogen and oxides of nitrogen, and leaving a residue of partially oxidised metals. The lead-rhodium compound has probably a similar constitution.

C. H. B.

## Mineralogical Chemistry.

**Analyses of Two New Amalgams and a Specimen of Native Gold.** By W. FLIGHT (*Phil. Mag.* [5], 9, 146—147).—A specimen of "native silver" from Kongsberg had the composition Ag 75.900, Hg 23.065, insol. 0.490 = 99.455, corresponding almost exactly with the formula  $\text{Ag}_2\text{Hg}$ . The amalgam from Moschelladsberg has the composition  $\text{AgHg}_2$ . Another specimen from the same locality had the composition Ag 92.454, Hg 7.195,  $\text{Fe}_2\text{O}_3$  0.033, CaO 0.055, AgCl 0.088, insol. 1.328 = 101.153, corresponding to  $\text{Ag}_2\text{Hg}$  (Ag 92.84, Hg 7.16). Both amalgams appear to be definite compounds. Silver, even when fused at a bright red heat, retains mercury with great tenacity.

A sample of washed native gold, in laminated grains and scales, from Punta Arenas, in the Straits of Magellan, had the composition Au 91.760, Ag 7.466, Cu 0.248,  $\text{Fe}_2\text{O}_3$  1.224 = 100.698.

C. H. B.

**Artificial Formation of the Diamond.** By J. B. HANNAY (*Chem. News*, 41, 106, and *Proc. Roy. Soc.*, 204, 1880).—According to the author the alkali-metals decompose the hydrocarbons present in paraffin spirit at high temperatures and pressures with separation of

carbon. When nitrogenous compounds were present a portion of the carbon was occasionally observed to separate in the form of diamond. Very strong tubes must be employed; the processes present great difficulties.

The best results were obtained with a mixture of 90 per cent. rectified bone-oil, 10 per cent. paraffin spirit, sufficient to three-fourths fill an iron tube  $20'' \times 4'' \times \frac{1}{8}''$  bore, and 4 grams of lithium.

The tube was kept at red heat for 14 hours. The author is of opinion that the diamond was produced in his experiments from the decomposition of a nitrogen compound, and not directly from the hydrocarbons.

M. M. P. M.

**Condition in which Sulphur exists in Coal.** By W. WALLACE (*Chem. News*, 41, 201).—It has been assumed that sulphur exists in coal chiefly, if not entirely, as iron bisulphide. Crace-Calvert has asserted that in some cases it is partly present as sulphates. The author shows that in some coals the sulphur chiefly exists as an organic compound. The following table shows the relative quantities of total sulphur and that existing as pyrites, assuming all the iron found in the ash to have been present as bisulphide:—

|                             | Total sulphur<br>per cent. | Sulphur as bisulphide<br>per cent. |
|-----------------------------|----------------------------|------------------------------------|
| Ell coal (Lanarkshire)..... | 0.91                       | 0.11                               |
| Main coal „ .....           | 0.60                       | 0.42                               |
| Splint „ .....              | 0.46                       | 0.14                               |
| Pyotshan „ .....            | 0.68                       | 0.17                               |
| Soft coal from Fife .....   | 0.93                       | 0.49                               |

The estimations of sulphur were made by Pattinson's method, and also by fusion with sodium carbonate and potassium nitrate. The Ell coal was found by Crace-Calvert's method to be free from sulphates, the others were not tested.

F. L. T.

**Existence of Zinc in all Primary Rocks, and in Sea Waters of all Ages.** By L. DIEULAFIT (*Compt. rend.*, 90, 1573—1576).—Zinc is found in all rocks of the primary formation. In the greater number of the 714 specimens examined it could be detected in 50 grams, and in all cases in 100 grams of the rock. It could also be detected in 50 grams of each of 155 specimens of non-fossiliferous, lustrous palaeozoic schists, and in the same quantity of 579 specimens from the lower fossiliferous deposits (silurian, devonian, carboniferous, and permian). In the case of sulphuretted schists, especially if containing coal, zinc could almost always be detected in 5 grams of the rock. It was likewise found in 50 c.c. of the last mother-liquors of the French salt-marshes. Taking into account only the quantity remaining in solution in these mother-liquors the waters of the Mediterranean contain at least 0.002 gram zinc per cubic meter. The muds of salt marshes, of old estuaries, and of estuaries still communicating with the sea, contain the same metal in such quantity that it can be readily detected in 50 grams. It can also be detected in 50 grams, indeed frequently in a much smaller quantity, of saline deposits, which the

author considers to be of estuarine origin, and the specimens of which, 128 in number, were mainly taken from the upper trias, and in a similar quantity of dolomitic rocks.

Blende is found in primary rocks, but especially at the point of contact of these with sedimentary deposits; the carbonate usually occurs in the latter. The deposits of Belgium and of Vieille-Montagne are in the carboniferous formation, those of Silesia are in the trias. Now zinc is readily detected in carboniferous schists and in saline deposits of the triassic period. Probably the zinc-compounds have been extracted from the primary rocks by the action of sea-water, then concentrated in estuarine deposits, afterwards redissolved by other water, and transported in a more or less pure condition to the places where they are now found. If the water contained no dissolved oxygen the zinc would be deposited as sulphide, if it were freely exposed to the air, as carbonate.

The author has, up to the present time, proved the existence in the primary rocks of lithium, strontium, barium, zinc, manganese, and copper, and has shown that these metals are concentrated in muddy deposits, which are always sulphuretted. When water containing dissolved oxygen or carbonic anhydride acts on the deposits, these substances undergo a series of changes terminating in the formation of the most stable compound, which will be different in different cases: for strontium, and especially barium, the sulphate; for manganese, the dioxide; for lead, the sulphide; for zinc and copper, the sulphide or carbonate, according to the quantity of air dissolved. These transformations will not all take place with the same rapidity, consequently the different minerals will be separated, and deposited at different points of the water's course. But the barium tends only to form the sulphate. The formation of this compound will therefore be gradual and continuous; it will be deposited at all points in the course of the water, consequently in company with all the various minerals, and also filling the gaps between the different metalliferous deposits, as we actually find it in lodes. It follows that all minerals having a barytic gangue have been formed from the primary rocks by one series of changes: hence they contain traces of rare metals, such as thallium, indium, and gallium, which also exist in those rocks. According to this view new metals should be sought for, not in mineral deposits having a barytic gangue, but in such rocks as the cupriferous schists of Mansfeld, Russia, and Bolivia, which have undergone but little modification.

C. H. B.

**Presence of Iron in the Dust Showers of Sicily and Italy.** By TACCHINI (*Compt. rend.*, 90, 1568—1569).—The dust showers which from time to time have fallen in Sicily and Italy contain spherical grains of meteoric iron; similar grains are found in the sand of the Sahara. In all probability the sand rains of Italy and Sicily are purely terrestrial phenomena, the sand being transported from the desert by cyclones.

C. H. B.

**Formation of Sulphuretted Mineral Waters.** By E. PLANCHUD (*Chem. News*, 41, 236).—Under the microscope the long delicate



threads usually supposed to be sulphur, found clinging to the stones in the neighbourhood of sulphur-springs, were found by the author to be composed of hollow cylindrical tubes matted together. Most of these tubes were filled with spores, which, when liberated, moved about with a rapid motion, finally came to rest, and developed hair-like processes similar to those from which they had been discharged.

The author filled three flasks with a solution of calcium sulphate; into one he put dead organic matter, into the other two hair-weeds from a sulphur-spring; one of the latter was boiled to destroy any life in it. All three flasks were then sealed hermetically, and left at rest under similar conditions; on opening it was found that only the flask containing the living hair-weeds gave off sulphuretted hydrogen. At the end of six months, however, the flask containing the dead organic matter had a faint smell of sulphuretted hydrogen, and hair-weeds were found in it on examination. Hence the author concludes the hair-weeds are the cause and not the effect of sulphuretted mineral waters.

F. L. T.

## Organic Chemistry.

**Transformation of Amylene and Valerylene into Cymene and Hydrocarbons of the Benzene Series.** By G. BOUCHARDAT (*Compt. rend.*, 90, 1560—1563).—Pure amylenes prepared from amylic alcohol by the action of zinc chloride, was converted into the dibromide, from which valerylene was obtained in the usual way, all the intermediate products being carefully purified. The valerylene (b. p. 45—50°) was converted into polymerides by heating at 250°. That portion of the product boiling between 170—190°, consisting mainly of divalerylene, was dissolved in twice its volume of carbon bisulphide, and bromine, also dissolved in carbon bisulphide, was added in the proportion of two equivalents to one of  $C_{10}H_{16}$ . After expulsion of the carbon bisulphide the bromides obtained were decomposed, partly by heat, and finally by an alcoholic solution of potash. The purified product of this series of reactions, boiling at 170—190°, was treated with sulphuric acid in order to destroy  $C_{10}H_{16}$ -hydrocarbons, which had escaped the action of the bromine. On distilling the portions not attacked by the sulphuric acid a hydrocarbon was obtained, which had all the physical properties of cymene. This liquid was treated with fuming sulphuric acid, neutralised with baryta, and, after separation of the barium sulphate, evaporated to dryness. The crystalline residue thus obtained consisted of barium cymenesulphonate, and a salt corresponding in composition to barium mesitylenesulphonate, but anhydrous. Substances derived from benzene have thus been obtained from amylic alcohol by successive removals of hydrogen. The author attempted to convert diamylene into cymene by the successive action of bromine and potash, but, like M. Tongollesoff, was unsuccessful.

C. H. B.

**Etherification of the Haloïd Acids.** By A. VILLIERS (*Compt. rend.*, 91, 62—64).—According to Berthelot the solutions of the haloïd acids may be regarded as solutions of the lower in the higher hydrates. As the temperature rises these hydrates are dissociated, the rate of dissociation being probably influenced by the presence of the alcohol. As a consequence the degree of dilution necessary to prevent etherification is increased, and the limit of etherification is also raised.

In those cases where no water is present at the commencement of the reaction, the limit of etherification, which is lower than for the organic acids, cannot be due to the water produced, for its amount is not sufficient to produce the observed effect. Probably the haloïd acids form with the alcohol compounds analogous to the hydrates, or to the crystalline compounds of the same acids with dulcete. The existence of such compounds is indicated, according to Berthelot, by the heat evolved when a haloïd acid is dissolved in alcohol, even under conditions such that no etherification takes place. The etherification is the result of equilibrium between the hydrates and the alcoholates.

C. H. B.

**Etherification of Hydriodic and Hydrochloric Acids.** By A. VILLIERS (*Compt. rend.*, 1563—1566).—Hydriodic acid acts more rapidly on alcohol than hydrobromic acid, and the percentage etherification is higher, the limits being—

|   | Ordinary temp. | At 44°. | At 100°.   |
|---|----------------|---------|------------|
| HI + 2C <sub>2</sub> H <sub>5</sub> O . . . . . | 71·4           | —       | 94·2 p. c. |
| HI + 10C <sub>2</sub> H <sub>5</sub> O . . . .  | 71·4           | 69·9    | 85·5 „     |

In the case of hydrobromic acid the limits are, at 44°, 59·5°; and at 100°, 80·0 per cent. of the acid used. With a certain degree of dilution of the alcohol, which increases with rise of temperature, and is greater for hydriodic than hydrobromic acid, all action ceases.

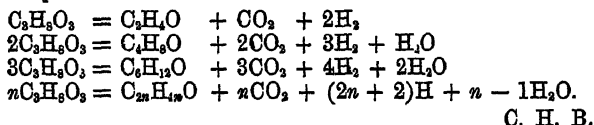
Hydrochloric acid is much slower in its action than the other haloïd acids or the organic acids, and the limits of etherification are much lower. The rapidity of the action, however, increases rapidly with rise of temperature, as does also the degree of dilution at which the action ceases. At ordinary temperatures the degree of dilution necessary to prevent etherification corresponds to HCl + 2H<sub>2</sub>O.

C. H. B.

**Compounds of Alcohols with Baryta and Lime, and the Products of their Decomposition.** By A. DESTREM (*Compt. rend.*, 90, 1213—1215).—When an alcohol is heated with caustic baryta or lime in closed vessels at 150—175°, the two bodies combine. The compound of ethyl alcohol with baryta decomposes at about 300°, giving almost equal volumes of hydrogen and ethylene, together, in all probability, with other products which, however, have not yet been isolated. The corresponding compound of amyl alcohol yields hydrogen and amylene. As a rule, the compound of the primary alcohols with baryta, when decomposed by heat, yield almost equal volumes of hydrogen and a hydrocarbon of C<sub>n</sub>H<sub>2n</sub> series corresponding with the particular alcohol. The lime compounds when similarly decomposed,

yield hydrogen and a liquid lighter than water, having an aromatic odour, but no volatile hydrocarbon is given off.

When glycerol is made into a paste with caustic baryta or quick lime, and heated at about 50°, the mixture at first liquefies, then contracts, and solidifies with considerable development of heat; finally it swells up, forming a granular powder. The compound thus obtained decomposes on heating into water, hydrogen, carbonic anhydride, and a liquid lighter than water, boiling between 75° and 210°. This liquid unites with sodium, forming a gelatinous compound; it also combines with baryta and with bromine. When distilled with phosphorus iodide it forms an iodide, which, when treated with silver acetate, yields an ethereal acetate. It is probably an unsaturated alcohol. Analysis of the fraction boiling between 160—170° gave numbers agreeing fairly well with the formula  $C_{10}H_{20}O$ . The liquid is probably a mixture of homologues of the formula  $C_nH_{2n}O$ , formed in accordance with the equations:—

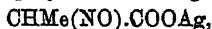


**$\alpha$ -Nitrosopropionic Acid.** By H. GUTKNECHT (*Ber.*, 13, 1116—1119).—It has been previously shown (*ibid.*, 12, 2290), that nitroso-methylethylketone,  $Me.CH(NO).CO.Me$ , gives on reduction the base,  $MeHC-N$  (m. p. = 88°, b. p. = 189°; the melting point was

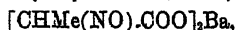


given as 80° in the paper referred to, which on treatment with bromine-water gives a brom-derivative crystallising in brilliant orange-red plates, which lose the whole of their bromine on exposure to the air. The free base is not acted on by nitrous acid, nascent hydrogen, acetic anhydride, or ethyl iodide.

Several derivatives of Meyer and Zublin's (*ibid.*, 11, 692)  $\alpha$ -nitrosopropionic acid have been prepared, including the silver salt—



the potassium salt,  $CHMe(NO).COOK + H_2O$ , the barium salt,



and the copper salt, containing water of crystallisation, which it loses at 110°, and then has the composition  $[CHMe(NO).COO]_2.Cu$ . In solutions of nitrosopropionic acid ferric chloride produces a brown-red, and cobalt nitrate a brown coloration. Nitrosopropionic acid, on reduction with tin and hydrochloric acid, gives alanine, and on oxidation with potassium permanganate in alkaline solution, ethylnitrolic acid.

T. C.

**Constitution of the Reduction-product of Succinic Chloride.** By A. SATZGEFF (*Ber.*, 13, 1061—1062).—The reduction-product of succinic chloride is not an aldehyde as previously stated, but the anhydride of normal hydroxybutyric acid, and belongs to Fittig's series of so-called lactones.

T. C.

**Amidolactic Acids.** By E. ERLIENMEYER (*Ber.*, 13, 1077—1079).—The amidolactic acid obtained by the action of ammonia on  $\beta$ -chlorolactic acid is identical with the amido-acid of Melikoff (*ibid.*, 12, 2228), whilst Cramer's (*J. pr. Chem.*, 96, 94) serine is isomeric with amidohydroxypropionic acid. T. C.

**Action of Phosphorus Pentachloride and of Zinc-Dust on Succinimide.** By A. BERNTHSEN (*Ber.*, 13, 1047—1050).—With the object of preparing piperidine,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{NH}$ , by the reduction of the imide of pyrotartaric acid,  $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\rangle\text{NH}$ , the author has made a preliminary investigation with the corresponding succinimide.

A dark green liquid is obtained by the action of phosphorus pentachloride on succinimide at a temperature not exceeding  $50\text{--}55^\circ$ ; this liquid is separable by means of light petroleum into a crystalline body and an oil. The former consists of flat prisms (m. p.  $145\text{--}148^\circ$  with partial decomposition); on distillation hydrochloric acid is evolved, but a portion appears to pass over undecomposed. It contains chlorine precipitable by silver nitrate; on heating with soda ammoniacal fumes are evolved, whilst on boiling with water and mercuric oxide, a microscopic crystalline precipitate is obtained, but no succinimide mercuric chloride. A base substance, not pyrroline, is produced on heating with amorphous phosphorus and hydriodic acid.

Pyrroline is obtained when succinimide is distilled with zinc-dust in a current of hydrogen, confirming C. A. Bell's results (*Ber.*, 13, 877).

T. C.

**Derivatives of the Toluidines.** By J. COSACK (*Ber.*, 13, 1088—1092).—*Orthotolylcarbamide*,  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ , is obtained by the action of potassium cyanate on orthotoluidine hydrochloride. It is easily soluble in ether and alcohol, moderately soluble in hot, but insoluble in cold water. It crystallises from alcohol in small plates (m. p.  $185^\circ$ ).

*Metatolylcarbamide*,  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ , obtained like the ortho-compound, crystallises from hot water in plates, and from alcohol in a mixture of plates and needles (m. p.  $142^\circ$ ).

*Metaditolylcarbamide*,  $\text{CO}(\text{NHC}_7\text{H}_7)_2$ , is prepared by heating moist metatolylurethane, or by heating toluidine with monotolylcarbamide at  $150\text{--}160^\circ$ . It is insoluble in water, but moderately soluble in hot alcohol, from which it crystallises in long needles (m. p.  $217^\circ$ ).

*Metatolylurethane*,  $\text{OEt CO.NH.C}_7\text{H}_7$ , is obtained by the action of ethylchlorocarbonate on metatoluidine. It is an oil which does not solidify at  $-47^\circ$ . It is easily soluble in ether and alcohol. When distilled in the moist condition it gives ditolylurea, alcohol, and carbonic acid. The ortho-compound has been previously described (*Ber.*, 12, 1479), whilst the para-derivative was obtained by Hofmann (*ibid.*, 3, 653).

*Orthotolylglycocine*,  $\text{C}_9\text{H}_{11}\text{NO}_2$ , was prepared by heating orthotoluidine chloracetate with water and toluidine. Its formation was not accompanied by that of any dye-stuff as stated by Staats (*Ber.*, 13, 137), nor did it form lance-shaped crystals, but leaflets (m. p.  $143^\circ$ ). Its copper salt,  $(\text{C}_9\text{H}_{10}\text{NO}_2)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , crystallises in very small needles.

The metatolylglycocine could not be obtained by the reaction corresponding to the above.

*Paraditolylamine* has been already obtained by Girard (*Annalen*, 140, 346), and also by Gerber (*Ber.*, 6, 446). The author has prepared the meta- but not the ortho-compound by similar reactions.

*Metaditolylamine*,  $\text{NH}(\text{C}_7\text{H}_7)_2$ , is a thick bright yellow oil (b. p. =  $319-320^\circ$ ), which on exposure to the air assumes a deep brown colour. It is easily soluble in ether and alcohol, but only sparingly so in acids, and is volatile with steam.

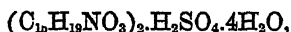
*Nitroso-paraditolylamine*,  $\text{N}(\text{C}_7\text{H}_7)_2\text{NO}$ , was obtained on adding potassium nitrite in slight excess to a hydrochloric acid solution of paraditolylamine. It crystallises in yellow needles (m. p.  $103^\circ$ ).

*Acetometaditolylamine*,  $\text{N}\text{Ac}(\text{C}_7\text{H}_7)_2$ , prepared by the method of Liebermann and Hörmann (*Annalen*, 196, 319), is a thick oil, which distils at  $324^\circ$  without decomposition under a pressure of 300 mm., and the distillate, which is the pure compound, solidifies to a mass consisting of colourless tables (m. p.  $43^\circ$ ). It is easily soluble in alcohol and ether, from which, however, it separates again in the liquid state.

T. C.

**Tropeïnes.** By A. LADENBURG (*Ber.*, 13, 1081—1088).—This is a continuation of the author's previous paper (*Ber.*, 13, 106).

*Hydroxybenzoyltropeïne*,  $\text{C}_{15}\text{H}_{13}\text{NO}_3$ , is obtained by evaporating equal parts of tropine hydrochloride and hydroxybenzoic acid with not too dilute hydrochloric acid. It consists of thin leaflets (m. p.  $226^\circ$ ), which are very sparingly soluble in water, rather more soluble in alcohol and ether, and easily soluble in acids and alkalis. The *hydrochloride*,  $\text{C}_{15}\text{H}_{13}\text{NO}_3\cdot\text{HCl}$ , crystallises in needles, which are easily soluble in water and in alcohol. The *sulphate*,



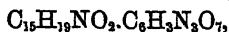
was also prepared, and the *platinochloride*,  $(\text{C}_{15}\text{H}_{13}\text{NO}_3\cdot\text{HCl})_2\text{PtCl}_4$ , forms orange plates, which are soluble in hot water, but insoluble in alcohol. The picrate, auro-chloride, and periodide are also described, as well as the results obtained on the addition of various reagents to a solution of the hydrochloride.

*Parahydroxybenzoyltropeïne*, obtained like the hydroxybenzoyl-compound, crystallises in colourless rhombic plates (m. p.  $227^\circ$ ), which are easily soluble in alcohol, but only sparingly soluble in water, and contain 2 mols.  $\text{H}_2\text{O}$ , which they lose at  $110^\circ$ . The free base is soluble in acids and in soda, but insoluble in ammonia. The *nitrate*,  $\text{C}_{15}\text{H}_{13}\text{NO}_3\cdot\text{HNO}_3$ , the *platinochloride*,  $(\text{C}_{15}\text{H}_{13}\text{NO}_3\cdot\text{HCl})_2\text{PtCl}_4$ , which crystallises from hot water in orange-coloured leaflets, and the *picrate*,  $\text{C}_{15}\text{H}_{13}\text{NO}_3\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , were also prepared, and the behaviour of the base towards various reagents described.

*Orthohydroxybenzoyltropeïne* has been previously described. Its *hydrochloride* crystallises in plates or prisms which are not easily soluble in water, whilst the *aurochloride* crystallises from hot water in golden leaflets.

*Benzoyltropeïne*,  $\text{C}_{15}\text{H}_{13}\text{NO}_2$ , is obtained like the preceding compounds, except that a little benzoic acid is added from time to time.

It crystallises in silky plates (m. p.  $58^{\circ}$ ), containing 2 mols.  $\text{H}_2\text{O}$ . Dried over sulphuric acid it falls to powder and loses  $\frac{2}{3}$  mol.  $\text{H}_2\text{O}$ , and the melting point is then  $37^{\circ}$ . It is a strong base, which dissolves easily in acids. The *nitrate*,  $\text{C}_{15}\text{H}_{19}\text{NO}_2 \cdot \text{HNO}_3$ , the *picrate*,



and the *platinochloride*,  $(\text{C}_{15}\text{H}_{19}\text{NO}_2 \cdot \text{HCl})_2 \cdot \text{PtCl}_4 \cdot 2\text{H}_2\text{O}$ , are described, as are also the reactions with various reagents.

*Phthalyltropine*,  $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_4$ , is very difficult to obtain, and only the *platinochloride*,  $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_4 \cdot 2\text{HCl} \cdot \text{PtCl}_4$ , which crystallised in needles, was prepared.

*Atropyltropine* or *anhydrotropine*,  $\text{C}_{17}\text{H}_{21}\text{NO}_3$ , is prepared like the previous compound from atropic acid, tropine, and hydrochloric acid. It could be obtained only in the form of an oil.

The *aurochloride*,  $\text{C}_{17}\text{H}_{21}\text{NO}_3 \cdot \text{HCl} \cdot \text{AuCl}_3$ , crystallises in small needles.

*Cinnamyltropine*,  $\text{C}_{17}\text{H}_{21}\text{NO}_3$ , was obtained from cinnamyl, tropine, and hydrochloric acid; it forms small leaflets (m. p.  $70^{\circ}$ ), which are easily soluble in alcohol and chloroform, but only sparingly soluble in water; it is a strong poison, but has at most only a slight mydriatic action. The *hydrochloride*, *platinochloride*, and *aurochloride* are described, and also the reactions with several reagents.

*Oxytoluyltropine* or *Homotropine*,  $\text{C}_{18}\text{H}_{21}\text{NO}_3$ .—This base, previously described, has not yet been obtained in the solid state. The *hydrobromide*, *hydrochloride*, and the *sulphate* have been prepared. As a mydriaticum (?) it is about as energetic as atropine, but its effects are developed much more rapidly; it is less poisonous than atropine. T. C.

**New Azo-Colours.** By J. H. STEBBINGS (*Chem. News*, 41, 117).—The compounds described are:—

*Azobenzene-trinitro-hydroxybenzene*,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}(\text{NO}_2)_3\text{OH}$ , crystallises in brown prismatic needles, with metallic lustre, from an alcoholic solution of picric acid, mixed with an aqueous solution of 1 mol. of diazo-benzene nitrate. The crystals explode at  $70^{\circ}$ . They are insoluble in cold, and sparingly soluble, with partial decomposition, in boiling water.

*Azobenzene-pyrogallol*,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}_2(\text{OH})_3$ , obtained by the action of diazo-benzene nitrate in aqueous solution or an alkaline solution of pyrogallol. The substance crystallises from glacial acetic acid and nitro-benzene in dark red-brown needles. Alcoholic solutions dye silk and wool gold colour.

*Azobenzene-hydroxycarboxyl-benzene*,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}_2(\text{OH}) \cdot \text{COOH}$ , an orange dye, obtained by the action of diazo-benzene nitrate on an alkaline solution of salicylic acid.

*Azobenzene-diamido-toluene nitrate*,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_6\text{H}_2(\text{NH}_2)_2\text{CH}_3$ , an orange dye, obtained by acting on an aqueous solution of diazo-benzene nitrate with  $\alpha$ -dinitro-toluene (m. p. =  $99^{\circ}$ ), filtering after an hour, dissolving in water and decomposing by ammonia.

*Diamido-azonaphthalene hydrochloride*,



a brown dye, obtained by the action of an aqueous solution of diazo-naphthalene hydrochloride on an alcoholic solution of diamido-naphthalene.

*Azobenzene-cresol-sulphuric acid*,  $C_6H_5.N : NC_6H_3Me(HSO_3).OH$ , forms brown needles with metallic lustre: obtained by decomposing with hydrochloric acid the product of the action of diazo-benzene nitrate on an alkaline solution of cresol sulphonic acid. M. M. P. M.

**Saliretone.** By P. GIACOSA (*J. pr. Chem.*, **21**, 221—227).—A new crystalline substance was obtained by heating saligenol and mannitol at  $100^\circ$ ; it did not appear to be a compound of saligeninol with mannitol, but rather a new condensation-product of saligeninol itself. To this body the author assigns the name saliretone. It was obtained in still larger quantities on substituting for the mannitol its equivalent weight in glycerol, and it was likewise obtained by heating saligeninol with methylol with a reversed condenser on the water-bath. The most efficient method for preparing this new body is to heat equal weights of saligenin and dry glycerol in *sealed tubes* (on heating in open vessels no saliretone, or but mere traces are obtained) for eight hours in boiling water; the saligeninol melts, and the whole mass is converted to a yellowish, homogeneous fluid. On adding water, a yellowish resinous mass separates, partly soluble in water on boiling, from which the saliretone crystallises out on cooling in rhombic plates and needles.

The product weighs only 2.5 per cent. of the weight of the saligenol employed, the greater portion remaining unchanged. The saliretone can be further purified by recrystallisation from hot water, or still more readily by solution in very dilute cold potash solution, and precipitation by hydrochloric acid. Purified saliretone,  $C_{14}H_{12}O_3$ , melts at  $121.5^\circ$ .

Saliretone gives no blue with ferric chloride; its dry crystals, however, like salicin and its derivatives, give a fine red colour with concentrated sulphuric acid. The fixed alkalis dissolve it easily, but it is reprecipitated in needles on addition of acids. Difficultly soluble in ammonia, and precipitated on dilution. After being melted, saliretone no longer crystallises; heated above  $140^\circ$ , it suddenly evolves gas, a distinct smell of salicylic aldehyde is observed, and a resinous body is left. Resinous bodies were also obtained by prolonged boiling with water, or by the action of chlorine or bromine.

Saliretone was heated at  $135$ — $140^\circ$ , until the weight was constant, the product extracted by ether evaporated, and the residue dissolved in dilute potash. The resinous precipitate thrown down by hydrochloric acid, washed, and dried at  $140^\circ$ , gave numbers agreeing, though not absolutely, with Piria's saliretin,  $C_7H_6O$  (*Ann. Chim. Phys.* [2], **69**, 318; and [3], **14**, 268). F. L. T.

**Formation of Hippuric and Benzoic Acids in the Animal Organism during Fever.** By T. WEYL and B. v. ANREP (*Ber.*, **13**, 1092—1098).—The normal urine of rabbits fed with milk and oats, contains hippuric acid, and mostly also free benzoic acid; during fever the quantity of free benzoic acid increases, whilst that of the hippuric acid diminishes; this does not depend solely on the deficiency of glycocoll. The absolute quantity of benzoic acid present during fever is not greater than in the normal condition, but the form in which it occurs is different.

The normal urine of a dog fed with fatty and albuminous food always contains hippuric acid, and mostly also small quantities of free benzoic acid. During fever the hippuric acid diminishes. In a healthy dog the greater part of the benzoic acid is converted into hippuric acid, whereas during fever the benzoic acid occurs in the free state to a greater extent than under normal conditions. T. C.

**Two New Dye-stuffs.** By L. VIGNON and J. B. BOASSON (*Ber.*, 13, 1060—1061).—A claim to priority of discovery of Biebrich scarlet over Miller (*ibid.*, 542) and Nietzki (*ibid.*, 13, 800). The authors have also obtained an additional series of dye-stuffs, one of which has been isolated in the pure state, and is prepared by the action of diazo-amidoazobenzene on  $\beta$ -naphtholsulphonic acid. It imparts to wool a more beautiful and solid colour than cochineal, the shade being more violet the higher the temperature at which the naphtholsulphonic acid has been prepared. This dye-stuff was introduced into the trade some months ago, under the name of Ponceau R.R. T. C.

**Camphor Chlorides.** By F. V. SPITZER (*Ber.*, 13, 1046—1047).—The nature of the products obtained by the action of phosphorus pentachloride on camphor depends on the amount of phosphorus pentachloride employed, and on the temperature (*Ber.*, 11, 1818; this Journal, Abstr., 1879, 168). If the mixture is kept cool, the only product of the reaction is camphor dichloride,  $C_{10}H_{16}Cl_2$  (m. p. =  $155^\circ$ ). The author is unable to confirm Pfaundler's statement, that an isomeric camphor chloride of lower melting point ( $70^\circ$ ) is obtained by the action of 1 mol. camphor on 2 mols. of phosphorus pentachloride, or that the chloride,  $C_{10}H_{16}Cl$  (m. p.  $60^\circ$ ) is obtained by heating equal molecules of the same reagents together: for he finds that Pfaundler's compounds are only mixtures, and that the chief product in every case is the dichloride (m. p.  $155^\circ$ ). When the reaction was carried out with the application of heat, a body containing less chlorine than  $C_{10}H_{16}Cl_2$  was obtained, but the monochloride,  $C_{10}H_{15}Cl$ , could not be isolated. T. C.

**Resins contained in Jalap.** By A. F. STEVENSON (*Pharm. J. Trans.* [3], 10, 644—645).—Resin of jalap consists of a mixture of convolvulin and jalapin. They may be separated by mixing the finely powdered resin with pure sand, and extracting first with ether, which dissolves the jalapin, and then with absolute alcohol, which dissolves the convolvulin.

*Jalapin*,  $C_{31}H_{50}O_{18}$ , obtained from the ethereal extract is a soft resin, soluble in ether, light petroleum, carbon bisulphide, oil of turpentine, chloroform, and hydrochloric acid.

*Convolvulin*,  $C_{31}H_{50}O_{18}$ , is obtained as a hard resin, odourless and tasteless, and insoluble in ether, light petroleum, carbon bisulphide, benzene, oil of turpentine; it is soluble in chloroform, water, and hydrochloric acid.

Sulphuric acid dissolves jalapin with a maroon colour, and convolvulin with a bright red. Both resins are soluble in potash and in ammonia.



Potassium chromate, permanganate, nitrate, or chlorate gives with jalapin an odour of rancid butter, and a brown colour; with convolvulin the same odour and an olive-green colour. Manganese dioxide gives with jalapin a dark-green colour, and with convolvulin a rose-pink colour.

L. T. O'S.

**Thapsia Garganica.** By C. BLANCHET (*Pharm. J. Trans.* [3], 10, 889—890).—The bark of the root of the *Thapsia garganica* contains, according to Martin, a rubefacient resin, tannin, starch, extractive lime, ligneous matter, and "thapsic acid;" the latter the author believes to be hydrochloric acid. The bark loses about 80 per cent. of its weight on drying, and whilst, when fresh, it yields 2 per cent. of resin, when it has been dried and kept for one year it yields only 5.55 per cent., this is due to the oxidation of the resin. The results of analysis are:—

|  | Dried bark.  | Fresh bark.  |
|--|--------------|--------------|
| Water.....                               | —            | 80.70        |
| Starch .....                             | 20.52        | 4.41         |
| Gum and colouring matters .....          | 7.32         | 1.47         |
| Resins .....                             | 5.55         | 2.15         |
| Matter soluble in alcohol and water .... | 1.38         | 2.42         |
| Elements not estimated .....             | 57.08        | 7.32         |
| Inorganic constituents.....              | 8.18         | 1.55         |
|  | <hr/> 100.03 | <hr/> 100.02 |

These results do not agree with those of Beslier (*Traité de Pharmacie*, 2, 192), who obtained from the fresh root 2 per cent. of resin, and from the dried root 15 per cent., while Nielli obtained 4.5 per cent. of resin from the fresh root, and only 5 per cent. from the dried.

The resin is soluble in alcohol (90°), ether, and carbon bisulphide; it is of a brown colour. When treated with boiling water it softens; it has an acid reaction.

The best method of extracting the resin from the bark is to treat it with hot water, dry, and cut it, and treat with boiling alcohol (90°) several times; the extracts are evaporated, the residue treated with cold alcohol (90°), and the solution after filtration, is evaporated to the consistency of honey. The residue has an aromatic odour, imparted to it by an essential oil, which is soluble in alcohol and ether, to which it imparts a blue colour; it is separated from its ethereal solution by shaking with water. The resin is very valuable as an irritant.

A resin is also obtained from "cleka," or "false thapsia," of a yellowish-brown colour, soluble in alcohol (90°), ether, and carbon bisulphide; it possesses no rubefacient properties.

L. T. O'S.

**Nigella Sativa.** By H. G. GREENISH (*Pharm. J. Trans.* [3], 10, 909—913, and 1013—1016).—The examination of the seeds of the *Nigella sativa* was undertaken to determine the relation between their chemical constituents and those of the other members of the subdivision Helleboræ on the one hand, and of the Pæoniæ on the other.

Previous examinations have been made by H. Reinsch (*Jahrb. f. Pharm.*, 4, 384), and Flückiger (*ibid.* [3], 2, 161).

A dark brown solid fat is extracted from the seeds by light petroleum, and a yellow volatile oil is obtained by distillation with water. The oil gives a red coloration when boiled with water, and a violet-red on addition of an alkali. The aqueous extract of the seeds is of a brown colour, and contains a mucilage, which is insoluble in alcohol, but soluble in hydrochloric acid. Alcohol extracts from the aqueous solution (1) a brown substance, soluble in alkalis, probably a decomposition-product of some tannin, and belonging to the class of phlobaphenes; (2) a pale yellow substance, soluble in benzene, ether, and chloroform; and (3) an amorphous brown substance, giving an odour of orcinol when boiled with hydrochloric acid. Water also extracts from the seeds a sugar, a yellowish-brown amorphous mass, containing phosphoric, hydrochloric, and sulphuric acid, and an albuminous body.

The alcoholic extract of the seeds consists of two portions, an oil containing a small quantity of white resin, and an amorphous mass, the alcoholic solution of which, on fractional precipitation with water, gave an oil coloured green by chlorophyll, a light-coloured precipitate, and an amorphous powder, insoluble in water, benzene, carbon bisulphide, and light petroleum; it is soluble in alkalis, and sparingly soluble in chloroform; from alcohol it crystallises in grey, microscopic prisms, melting at  $205^{\circ}$ . A few drops of the alcoholic solution added to water produce a considerable frothing on shaking; the alcoholic solution gives with ferric chloride a yellowish-green coloration. Sulphuric acid gives a reddish coloration, changing to yellow rose-red, and finally violet-red. Sulphuric acid and sugar give a violet-blue colour. The author calls the substance *melanthin*, its formula being  $C_{20}H_{28}O_7$ . When boiled with hydrochloric acid melanthin is decomposed into a sugar, and a substance sparingly soluble in water, *melanthigenin*,  $C_{14}H_{22}O_2$ . It forms microscopic crystals, and gives colour reactions similar to melanthin.

Melanthin may be distinguished from saponin and digitonin by its being sparingly soluble in water, and easily soluble in alcohol; the aqueous solution of digitonin, when boiled with dilute acid, also gives a red coloration.

From parillin and parigenin melanthin may be recognised by being more sparingly soluble in water, by its property of frothing, its reaction with sulphuric acid, and by its rapid decomposition when boiled with dilute acid.

Helleborein is more soluble in water than melanthin, and its decomposition product, *helleboretin*, dissolves in alcohol with a red colour, and gives a brown coloration with sulphuric acid. Melanthin may be distinguished from helleborein by being less soluble in chloroform, and by the facility with which it is decomposed by dilute acids.

Caustic soda extracts from the seeds a black powder consisting of an impure albuminoid; the extract does not contain any alkaloid.

The solid fats contained in the seeds consist of myristic and stearic acid.

A quantitative analysis of the seeds is given.

L. T. O'S.  
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**Emetine.** By PODWYSZOTZKY (*Pharm. J. Trans.* [3], 10, 642—643).—Ipecacuanha is extracted with ether and light petroleum to remove the oil, fat, and colouring matter. The latter forms a purple-red compound with alkalis. From the barium compound an acid is obtained, crystallising from chloroform in straw-coloured needles, and called *erythrocephalein*.

The residue left on extraction with ether is dried and treated two or three times with alcohol (85°); the extract is evaporated to a syrup, and a concentrated solution of ferric chloride added in quantity sufficient to combine with all the tannin. To the solution excess of dry sodium carbonate is added, until a chocolate colour is produced, and the mass is extracted two or three times with hot light petroleum, until all the emetine is dissolved. On cooling the concentrated solution, emetine separates out as a white precipitate. It is precipitated from more dilute solutions by blowing air through them; a more expeditious method for separating the alkaloid is to treat the powder with sufficient hydrochloric acid to make a paste, add ferric chloride and sodium carbonate, leave the mixture at rest, and exhaust it with ether. The ethereal solution is shaken with water containing a small quantity of an acid, which dissolves the alkaloid; and the aqueous solution is treated with excess of soda, and boiled with petroleum spirit, from which the alkaloid is separated as before, and dried over sulphuric acid.

Emetine (m. p. 62—65°) is soluble in ether, chloroform, ethyl acetate, methyl, ethyl, and amyl alcohol, carbon bisulphide, oil of turpentine, essential oils, fatty oils, fats, and oleic acid. It is very sparingly soluble in water; it has a bitter and somewhat astringent taste, and is coloured yellow by exposure to sunlight. If a concentrated solution of emetine in light petroleum is evaporated very slowly on filter-paper, it forms acicular crystals round the edge; its reaction is strongly alkaline. Its salts are all soluble in water except the tannate, an amorphous white powder.

When treated with concentrated sulphuric acid, emetine gives oxalic acid; heated at 150° with dilute sulphuric acid under pressure, it was converted into a blackish-brown substance.

A drop of sodium phosphomolybdate in sulphuric acid, brought into contact with a particle of emetine, colours it brown, and on adding a drop of concentrated hydrochloric acid, the colour is changed to indigo-blue.

L. T. O'S.

**Preservation of Solutions of Palmelline.** By T. L. PHIPSON (*Chem. News*, 41, 216).—It is found that ether, which has no solvent action on palmelline and does not affect its composition nor coagulate it, may be used with success to preserve the liquid for an indefinite period. It has been found that salicylic acid partially destroys its optical properties.

F. L. T.

**Taraxacum Root.** By J. B. BARNES (*Pharm. J. Trans.* [3], 10, 849).—Experiment proves that the alcoholic extract of taraxacum root is superior to the extract of the pharmacopoeia. It is entirely free from albumin and inulin, and on evaporation to dryness leaves a bright yellow hygroscopic powder with an intensely bitter taste and

soluble in water. Cold water does not extract the bitter principle from the root. By extracting the dried root with alcohol, and distilling the solution, an oil is obtained, soluble in ether. On evaporating the ethereal solution, a tasteless green oil is obtained. L. T. O'S.

**Yerba Mausa.** By J. U. LLOYD (*Pharm. J. Trans.* [3], 10, 666—667).—This plant, the *Anemopsis Californica*, when bruised, exhales a pungent, disagreeable odour. Its taste, which is derived from a volatile oil, is aromatic and peppery. The oil is extracted by distilling the roots with water.

The essential oil is heavier than water, of a yellow colour, highly refractive, and is soluble in alcohol, ether, carbon bisulphide, and chloroform. When treated with sulphuric acid, it gives a dark red liquid, soluble in alcohol and chloroform with a red colour, insoluble in ether. When gently agitated with aqua regia it first gives a blue coloration, and is afterwards decomposed, yielding a brown resinous mass. Treated with hydrochloric acid in the same manner it gives a deep blue colour, which on standing changes to violet, purple, and finally brown. By exhausting the root with alcohol, and evaporating the extract, an oil and a gummy substance are obtained.

The oil is heavier than water; its odour and taste are the same as those of the root. It is soluble in ether, alcohol, chloroform, and carbon bisulphide; from the last solution a red flocculent precipitate separates out, the supernatant liquid having a light colour similar to the essential oil. The precipitate is astringent and deliquescent.

The gummy substance purified from the oil by washing with carbon bisulphide is a brown granular substance (m. p. 125—150° F.) having an astringent and peppery taste; it is soluble in dilute alcohol and in glycerol. By treating the dried gum with water, a flocculent residue is obtained, soluble in glycerol and in alcohol, insoluble in chloroform, ether, and carbon bisulphide; it gives a black precipitate with ferrous sulphate. The filtrate from the residue is colourless, astringent, gives a black precipitate with ferrous sulphate, and with Fehling's solution a heavy red precipitate. When the residue insoluble in water is triturated with ether and chloroform, a portion dissolves leaving an astringent deliquescent substance, which appears to be the same as the substance which separates from the solution of the oil in carbon bisulphide.

The residue from the alcoholic extract when treated with water and acidulated water, yields astringent solution giving reactions with Fehling's solution.

All attempts to extract any wax or resin have failed.

L. T. O'S.

**Tayuya.** By D. PARODI (*Pharm. J. Trans.* [3], 10, 667—668).—*Tayuya* (*Trianosperma ficifolia*) a plant of the family of the Cucurbitaceæ, gave on analysis the following results:—

|  |       |
|--|-------|
| Water .....                                  | 11.75 |
| Glucose .....                                | 0.84  |
| Crystalline substance soluble in alcohol.... | 0.24  |
| Resin .....                                  | 1.17  |
| Starch.....                                  | 17.23 |
| Organic acids, woody fibre .....             | 57.39 |
| Silica .....                                 | 1.02  |
| Lime .....                                   | 4.71  |
| Magnesia .....                               | 3.12  |
| Iron and alumina .....                       | 1.23  |
| Potash and soda .....                        | 1.30  |

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Trianospermin, a crystalline body, is obtained from the root by treating the alcoholic extract with water, which precipitates the resin. To the solution lead acetate is added, and the filtrate freed from excess of lead by sulphuretted hydrogen, is again filtered and evaporated, whereupon potash and soda salts crystallise out. Alcohol is added to the mother-liquor to separate the gum, and the sugar by addition of ether. The solution is evaporated to dryness, the residue dissolved in water, and the solution precipitated with tannin. The precipitate is mixed with magnesia, dried and exhausted with alcohol. On evaporating the extract to the consistency of syrup, and shaking it with ether, the *trianospermin* is dissolved, and crystallises out on leaving the solution at rest. The solution separated from the ether contains trianospermin and a bitter substance; the former crystallises on addition of alcohol.

Trianospermina forms colourless and odourless needles, having a pungent taste and alkaline reaction, and soluble in water, alcohol, and ether. It volatilises when heated, and gives precipitates with lead acetate and platinum tetrachloride. L. T. O'S.

#### Cholecamphoric Acid and its Relation to Cholanic Acid.

By P. LATSCHEINOFF (*Ber.*, 13, 1052—1060).—Cholecamphoric acid obtained by the oxidation of cholic acid (*Ber.*, 12, 1627), has in aqueous solution a specific rotatory power of  $[\alpha]_D = +56^\circ 10'$ , the amount of which is not influenced by the degree of concentration; in glacial acetic acid  $[\alpha]_D = 57^\circ 50'$ . A table is given showing the solubility of the acid in water and in alcohol of various strengths.

Cholecamphoric acid when treated with sulphuric or hydrochloric acid, loses water and gives the cholanic acid obtained by Tappeiner (*Annalen*, 184, 216) from cholic acid thus:—



This change is, however, accomplished more easily by means of etherification either by the action of a current of hydrochloric acid gas on the alcoholic solution of cholecamphoric acid, or by the action of ethyl iodide on the lead salt in presence of alcohol. In both cases the products are the same, viz., ethyl cholanate, tetrethylcholanic acid, and free cholanic acid.

*Ethyl cholanate*,  $C_{20}H_{36}EtO_6$ , is a substance resembling wax in appear-

ance (m. p. 50—60°). It is odourless when cold, but when warmed smells like burning sealing wax.

*Tetraphylcholic acid*,  $C_{40}H_{82}Et_4O_{12}$ , crystallises on slow evaporation in long needles (m. p. 130—131°), which are easily soluble in alcohol or ether, but insoluble in water. Its salts are precipitated from aqueous solution by means of common salt in the form of bulky gelatinous precipitates. They are also precipitated by ammonia, and excepting those of potassium and sodium, are only sparingly soluble in water. The acid on saponification gives cholic acid. In addition to Tappeiner's description of this acid (*loc. cit.*), which is in most respects confirmed, the author makes the following remarks:—The impure acid is easily soluble in ether, whereas the pure compound is only sparingly soluble, although more so than cholecamphoric acid. The barium salt separates from the boiling solution in the crystalline and not in the amorphous state, and contains not 7 but 10 mols.  $H_2O$ . Cholic acid when heated with nitric acid of sp. gr. 1.37 takes up the elements of water, and forms cholecamphoric acid, this transformation taking place even more easily than the inverse reaction referred to above. The choloidanic acid obtained by Tappeiner (*loc. cit.*) by the action of nitric acid on cholic acid, is nothing more than impure cholecamphoric acid, and this is the sole product. This explains why cholic acid when treated with nitric acid gives cholecamphoric acid, whereas on oxidation with potassium permanganate it gives only cholic acid. The author considers that the formulæ of cholic and cholecamphoric acids are  $C_{16}H_{14}O_4$  and  $C_{16}H_{16}O_4$  respectively, and not the double of these. T. C.

**Globulin-substances in Potatoes.** By P. ZÖLLER (*Ber.*, 13, 1064—1065).—Potato filaments contain a globulin-substance very similar to myosin. Potato juice also contains albuminous substances belonging to the class of globulins. These bodies are soluble in a dilute solution of salt, but insoluble in a strong solution or in pure water. This to a certain extent explains the influence of salt on the growth of the plant, for if salt be added to the soil, the aerial portion of the plant is richer in nitrogen, and grows more rapidly, but at the expense of the subterranean portion. T. C.

**Products of Action of Hydrochloric Acid on Albuminoids.** By J. HORBACZEWSKI (*Chem. Centr.*, 1879, 778—781, and 792—797). The various nitrogenous substances were digested, usually for 2—3 days, in flasks fitted with inverted condensers, with hydrochloric acid (generally 1:1) and stannous chloride.

Horn yielded aspartic and glutamic acids, leucine, tyrosine, ammonia, and sulphuretted hydrogen.

Human hair yielded the same products, but only about 0.1 per cent. of aspartic acid.

Gelatin yielded glutamic acid, leucine, glycocine, ammonia, and sulphuretted hydrogen.

Hard skin of oxen and horses yielded the same products as gelatin with traces of tyrosin. M. M. P. M.

## Physiological Chemistry.

**Feeding Experiments on Swine.** By E. v. WOLFF and others (*Bied. Centr.*, 1880, 183—191).—These experiments were made with a view of comparing the effects of food chiefly containing vegetable albumin with that containing similar quantities of animal albuminoids. The subjects of the experiments were pigs, a certain number of which were fed on boiled mashed potatoes, together with split peas; another lot on flesh-meal and starchy food, a little linseed oil being added to the food of the former lot in order to equalise the fat contained in the flesh-meal. The chemical constituents of each class of food were as equally balanced as possible. In the beginning, the amount of flesh-meal was about one-half, increasing to three-fourths the total food, and finally two of the animals were fed altogether upon it.

The observations were somewhat interfered with by the death of two of the animals, and the necessity of substituting others for them. The duration of the experiments was in both cases 182 days. During this period the swine which received the flesh-meal gained on an average per day per head 496 grams, whilst those fed on peas, &c., increased 466 grams; the amount of food actually digested to produce 100 kilos. of live weight was in the first case 319 kilos., and in the second 346 kilos., not a large difference, and which would be found smaller if account were taken of several days on which those fed on peas were not in good feeding order, which accident did not occur to those on flesh-meal. In fact, the difference in that case is so slight, that the authors consider the chief value of the flesh-meal consists in its being an agreeable addition to more bulky fodder, enabling the animals to get the same nourishment in less bulk, and that when fed upon it, their appetite is more regular. The price of flesh-meal is an important factor in the question for the practical farmer. (Compare this vol., p. 415.) J. F.

**Assimilation in Sheep of Various Ages.** By H. WEISKE and others (*Bied. Centr.*, 1880, 268—280).—The chief object was to ascertain the difference in the assimilation with increasing age of the various mineral constituents of fodder. For this purpose two lambs of about four months old were fed on meadow hay and split peas until they were two years old. The results of the assimilation of the mineral as well as of the organic constituents are given in an extensive series of tables, from which it appears that lambs assimilate during the first year a tolerably constant amount of chlorine and soda, but a gradually increasing amount of lime, magnesia, and phosphoric acid, whilst potash appears to be assimilated in proportion to the growth of the wool. Of these the potash, phosphoric acid, and the lime are the most requisite constituents.

At the age of two years a very small amount of mineral substances is apparently required, of which the alkalis still predominate. The absorption of phosphoric acid and lime has now almost ceased, whence it may be assumed that at two years the bones are fully developed.

A. J. C.

**Absorption of Lime Salts.** By L. PERL (*Bied. Centr.*, 1880, 308).—The amount of lime secreted in the urine of a dog weighing 22 kilos., to which 7·10 grams of calcium chloride had been given daily with the food, was increased from 0·135 gram to 0·325 gram per day and the chlorine by 6·14 grams. These results were confirmed by another series of experiments in which the greater part of the lime introduced as calcium chloride was found in the fæces, but the whole of the chlorine in the urine. The calcium chloride had probably been decomposed by the alkaline secretion of the bowels into sodium chloride and calcium carbonate.

A. J. C.

**Effect of Feeding-Cakes on Milk Production.** By G. I. HUNGEFELD (*Bied. Centr.*, 1880, 233).—The author carried out his experiments at the Royal Veterinary School in Holland upon five cows, which for a while received 1 kilo. of maize cake in addition to their ordinary fodder, and in the second period the same quantity of linseed cake. There was no difference in the quantity of milk; the mean of six analyses showed the following variations in composition percentages:—

|             | Water. | Dry sub. | Fat. | Milk-sugar. | Albumin. |
|-------------|--------|----------|------|-------------|----------|
| Maize ....  | 86·35  | 13 65    | 4 40 | 4·13        | 5·12     |
| Linseed.... | 89·915 | 14·085   | 4·56 | 4·01        | 5·515    |

Both kinds of food produced milk of excellent quality, but the author states that the milk, butter, and cheese, after the feeding on maize, were of a more agreeable flavour than after the other fodder; the same should hold true of the flesh of maize-fed sheep.

J. F.

**Activity of Bees.** By E. ERLÉNMEYER and PLANTA-REICHENAU (*Bied. Centr.*, 1880, 191—193).—This paper is a sequel to former reports on a similar subject (see this vol., 415), being further experiments made to ascertain whether the wax secreted by bees is derived from the sugar and other hydrocarbons which are found in the nectar of the flowers, or from such nitrogenous matters as exist in the pollen. A healthy swarm was bought in February, well cared and fed, and at the beginning of the experiments was in a very healthy condition. A determined number of the bees were carefully weighed, and with the queen transferred to the experimental hive, which was furnished with all appliances requisite for carrying out the experiments. The food was weighed in tared capsules; before the weighing of the swarm 50 of the bees were killed with chloroform vapour, and used for fat and nitrogen determinations. Each experiment lasted four days and four nights, and for a whole day the animals were confined to the hive.

The bees were first fed with a solution of sugar-candy, and a remarkable yield of wax was the result. The suggestion was made that the albumin in their bodies contributed to it, but both the nitrogen and the fat were the same before and after the experiment. A second trial was made by feeding the bees on honey, but the quantity of wax produced was less. Further observations, extended over longer periods, were made with a view to see what effect temperature would have on the production of wax. The first, made during favourable



weather on sugar-candy solution mixed with 1 per cent. of wheat flour, gave very good results; the second, carried on simultaneously on honey and wheat flour, gave good, but still inferior results; the third, with the same food as the first, but in less favourable weather, gave a much inferior yield; in another experiment the small proportion of 0.22 per cent. dry gelatin was added to the sugar solution with unsatisfactory results, whilst a much larger proportion of gelatin,  $1\frac{1}{4}$  per cent., added to honey produced a very large amount. When, however, the quantity of gelatin was increased to 5 per cent., and when a mixture of 20 parts peptone and 20 parts honey was employed, the bees refused their food altogether, and most of them died. A mixture was made of 1.18 parts glutinous peptone, 100 parts sugar, and 60 parts rose-water; it was all eaten, but neither honey nor wax produced; the bodies of the bees were distended, their honey-bags full, but their stomachs empty. A mixture of 342 grams sugar-syrup and 28 grams egg-albumin was also quickly consumed, but no honey or wax obtained; a similar mixture of egg-yolk (24 to 414 sugar syrup) produced a small proportion of wax only. As general results the authors believe that the food of bees should not be highly nitrogenous, and that beeswax is formed from non-nitrogenous substances, especially sugar.

Erlenmeyer is further of opinion that the fatty portions of the bees' bodies are formed solely from hydrocarbons, the albuminoids only playing the part of nourishment to the active organs, keeping them in working order and supplying waste. J. F.

**Extractives from Muscles.** By B. DEMANT (*Chem. Centr.*, 1879, 790).—The amount of creatine (and creatinine) increases rapidly in the muscles of pigeons kept without food. Xanthine and hypoxanthine decrease regularly in the muscles of healthy pigeons, but increase during long-continued inanition. Lactic acid decreases during inanition. M. M. P. M.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of the Galvanic Current on Bacteria.** By F. COHN and B. MENDELSON (*Bied. Centr.*, 1880, 226—227).—The authors carried out their experiments to verify the assertion of Schiel, that the galvanic current prevented the development of bacteria.

The results were that a feeble current from one pair of elements had no perceptible effect; a current from two elements rendered the solution inactive at the positive pole; a current from five continued for 24 hours completely sterilised the whole solution, and deprived it of its power to infect another solution. The solution at the positive pole was first affected, with the stronger current the liquid became acid at the positive and alkaline at the negative pole. The induction current had no perceptible effect on the bacteria. J. F.

**Effect of Putrefactive Changes on Bacteria.** By WERNICH (*Bied. Centr.*, 1880, 224—226).—In all solutions containing bacteria

a time arrives when they cease to propagate, and after a longer time they lose their power to induce further life in fresh nutritive solutions. This admitted fact leads to the belief that the putrefaction induced by bacteria produces substances which are poisons to these organisms.

Experiments were made on meat-extracts of various ages with phenol, skatole, indole, and other putrefaction-products, all of which were found to exercise an injurious effect on bacteria; moreover substances most disposed to putrefaction were easily preserved from it by means of any of them in fresh solutions which were purposely impregnated. The addition of trifling quantities of these matters promptly caused inactivity of the bacteria, and the author considers he has fully proved the truth of Baumann and Nencki's propositions on the subject.

The experiments in question lead to the solution of a highly interesting problem in pathology. The author says that the same or similar operations are carried out in the progress of septic diseases; the supposition that the organisms which are the cause of infectious diseases give rise to products which eventually cause their own distinction is the only way in which the progress of these diseases can be properly comprehended. Many sicknesses, such as smallpox, measles, scarlet and relapsing fevers, which are now generally ascribed to the presence of bacteria, progress so peculiarly and take such a regular course that one is forced to believe that, with the cause of the malady, its own distinctive poison is produced in the same manner as in the experiments here noted.

J. F.

**Bacteria in the Atmosphere.** By MIFLET (*Bied. Centr.*, 1880, 227—228).—The author reports the results of numerous experiments on the germs of bacteria contained in the air, and draws the following conclusions therefrom:—

That the air contains numerous fertile germs, which can be gathered by the experimentalist and systematically propagated and classified; that not only does the air contain the fertile germs of well-known species, such as micrococci and bacilli, but of other peculiar species which are not classified; but that on the other hand the germs of the bacteria of ferments, the *Bacterium termo*, the ferment of putrefaction, spirilli, &c., have not been recognised. Air drawn through soil has sometimes shown the presence of bacteria germs; but on the other hand the air from the rooms of a crowded hospital for spotted typhus fever was found to be quite free, probably in consequence of excellent ventilation and disinfection. Air taken from above a sink was rich in fruitful germs.

J. F.

**Atmospheric Bacteria.** By P. MIGUEL (*Compt. rend.*, 91, 64—67).—The number of bacteria present in the air is very small in winter, increases in spring, is still higher in summer and autumn, and decreases rapidly during hoar frosts; during dry periods the number of bacteria is high, that of mould-spores is low; in wet periods, the number of bacteria is very low, that of mould-spores is high. The author has endeavoured to determine the number of bacteria in a given volume of air, but with no definite results. On certain days during the winter 200 litres of air produced no change in solutions very liable to

alteration; in some cases air taken from quiet rooms was without effect in quantities less than 30 litres; in the case of air taken near sewers 1 litre was sufficient. Comparing the amount of bacteria in the air with the prevalence of zymotic diseases, the author concludes that an increase in the amount of bacteria is apparently followed, after an interval of eight days, by an increase of contagious and epidemic diseases, but the evidence is not sufficient to definitely settle the question. Other experiments lead to the conclusion that the vapour of water rising from the soil, from rivers, or from masses in full putrefaction, is free from germs; that the gases evolved from decaying substances, and the air passed over putrid meats are free from germs, provided that the putrefying substance is as moist as soil taken 0.3 m. from the surface. The author has inoculated many living animals with bacteria of various kinds, but without any physiological effects.

C. H. B.

**A Digestive Ferment of the Juice of the Fig-tree.** By BOUCHUT (*Compt. rend.*, 91, 67—68).—The milky juice which is found in small quantity in the common fig-tree, was collected in Provence in the month of April. 5 grams of the partially coagulated substance, consisting of a syrupy liquid, and a white, sticky, resinous, elastic, aromatic coagulum were mixed with 60 grams distilled water, 10 grams of moist fibrin added, and the mixture kept at a temperature of 50°. In less than 24 hours the fibrin was completely digested, leaving a small quantity of white, homogeneous residue. A further quantity of 10 grams, then 12, then 15, in all 90 grams of fibrin were added in the course of a month. Each successive quantity was completely digested in 24 hours, and each left a white residue, the composition of which has not been determined. The liquid showed no signs of fermentation or putrefaction.

C. H. B.

**Chemical Changes in Nitrogenous Substances during Fermentation.** By M. DELBRÜCK and others (*Bied. Centr.*, 1880, 217—222).—This is an endeavour to estimate quantitatively the amount of yeast formed during fermentation by examination of the mash before and the filtrate at the end of the process. The authors proceed from the standpoint that the mash is a solution of nutritive material, from which the yeast-cells in their growth abstract the matter necessary for their development, and that consequently the difference in the amount of this material found at two examinations is an exact measure of the yeast produced, the chemical composition of the yeast itself remaining constant. The sugar contained in the mash cannot be taken as a standard, as it splits up into alcohol and carbonic anhydride, and these do not remain in the yeast. It is otherwise, however, with albuminous matters, of which the yeast shows a percentage of 60 per cent. in the dry substance, these can be taken as an exact measure of the yeast production.

The difficulty of directly estimating albuminous bodies leads the authors to measure them by means of one of their constituents, nitrogen, and they find the process exceedingly accurate: for example, in one experiment they found for 100 parts of nitrogen, which was contained in the sweet mash, undissolved in the ground malt 46.2 parts,

dissolved in the filtrate 53.8, total 100 parts; and after fermentation undissolved in the grains and yeast 64.8, dissolved in the filtrate 35.2, total 100 parts, showing that 18.6 parts of nitrogen had passed from the soluble to the insoluble state. A series of experiments was made with like results, and the authors formulate the following rule. The absolute quantity of yeast produced in a mash is independent of the dissolved sugar, but depends directly on the amount of soluble nitrogenous matter. The authors discuss the supposition that a combination of the alcohol with the acid might lead to production of albuminoids, but dismiss it as untenable, having found that a quantity of about 1.2 per cent. lactic acid caused very little separation of those substances.

To settle the question they took 100 c.c. of clear filtered sweet mash, and mixed it with 15 c.c. of 90 per cent. alcohol, so that the mixture contained about 12 per cent. of alcohol. Many hours' observation failed to show any results which would tend to lessen the value of the proposed mode of estimation. Another important point in regard to fermentation which the authors propose to decide is the period at which the yeast cells are formed, and they believe that in this matter also the estimation of the soluble nitrogenous matter is a valuable indicator, as shown by the following experiment: the mash was of potatoes with 4 per cent. of barley malt, and they found that at the beginning of the head fermentation 33 per cent. of the soluble had become insoluble, at the end of the head fermentation 35.4 per cent., and at the complete termination of the fermentation 36.1 per cent., the vast bulk of the yeast having been formed before the visible working commenced. They draw the conclusion that the formation of yeast cells has practically no connection with the visible working of the mash.

Another experiment had an unexpected result: the mash was the same as in the former instance, but the temperature at which the operation was carried out was 2° Reaumur lower. After the top fermentation was over there was a considerable increase in the amount of soluble nitrogenous matter existing in the filtrate, as much as 7.5 per cent. which had previously become insoluble reverting to the soluble condition. The authors believe that if the temperature is too low there is a decomposition of the yeast, but they have not fully investigated this aspect of the subject. J. F.

**Seed Production of Red Clover.** By G. HABERLANDT (*Bied. Centr.*, 1880, 199—201).—Every farmer who raises red clover for the sake of the seed is aware of the uncertainty of its produce. The quality of the crop frequently suffers from the unequal ripening of the seeds, and this in a far greater degree than is the case with other field crops. Darwin's researches have shown clover to be one of those plants whose fructification depends on the visits of insects. The florets of any individual head of blossom are not all at one time in a fit state to profit by the visit of those insects, the lower florets expanding first, the upper later, and when these are in full bloom the lower have decayed, or at least are on their way to decay; when the crown of the stalk has bloomed the florets are weakly and unattractive to insects.

The author's researches confirm this view. A certain number of the ripe flower-heads, all grown under precisely similar conditions, were examined as to the proportion of fruitful and sterile florets, and it was found that in the upper portion the fruitful seeds predominated; whilst the reverse was the case in the under portion of the flower head. Some seeds were barren in the upper florets, but they were too few to affect the proportion.

Under favourable circumstances the greater part of the florets would be fructified, but those circumstances rarely occur, and for a rarely successful crop of seed, a vigorous and quick bloom, and an active visitation of insects is necessary; whilst bad results are to be expected from dull rainy weather, which retards blossoming and is unfavourable to insect life. The author suggests the encouragement of bees about clover farms, but can propose no other remedy for the unequal blooming of the flowers than a careful selection of the seed. J. F.

**Germination of Beet Seeds.** By P. PUTTE (*Bied. Centr.*, 1880, 196—199).—The author's object in the experiments reported was to ascertain the effect of steeping the seed of the sugar beet in manure materials. During the previous year, he had made experiments with potassium nitrate, which was employed to the amount of  $2\frac{1}{2}$  times the weight of the seeds, either in fine powder applied, or in the form of a solution of the strength of 22° Baumé. Seeds steeped for 24 hours germinated easily and quickly; on the appearance of the seedling leaves they took a fine colour, and developed more strongly than seed which had not been so treated. Superphosphate has been tried in concentrated solution, but is unsuitable by reason of its acid and corrosive nature, and the difficulty of drying the seeds sufficiently for the sowing machine. If employed at all it should be in the form of dried powder.

The germination of the beet seed begins between 6—7° C.; at this temperature it takes about 20 days to appear above ground. At less than 6° the growth is arrested, to recommence when the temperature is raised; it is, therefore, necessary to sow in April. In the beginning of the month the midday heat alone is useful, and it does not penetrate deep enough into the soil, hence the necessity of shallow sowings of this seed. It also requires a large amount of moisture, and if sown deep or too early the tender shoots are unable to pierce the thick layer of earth which covers it.

The author has had good results in practice from 48 hours' steeping in liquid stable manure, and drying sufficiently to sow. Instead, however, of spreading the seeds to dry they may be gathered in heaps and allowed to heat sufficiently to start the germination: in 5 or 6 days the radicle appears, and sowing should be immediately proceeded with. In well prepared ground the growth proceeds without interruption, and in less than 14 days, if sown in the middle of April, there is a well grown crop of seedling.

No better cultural instructions can be given for beets than those which are followed successfully with potatoes. The choice of soil, manures, and all conditions are similar, and for both a late vegetation is undesirable, as it diminishes the time for coming to maturity, until

which, the full quantity of sugar is not obtainable. Sugar can be found at all stages in the growth of the beet, but it is much less in the growing plant than when the cells are fully formed and their production has ceased. In the plains of Algeria the beet is indigenous and an annual; there is no repose in vegetation, no need for the plant to store up sugar for future use; this is probably the cause of the small yield of sugar in the beets of Spain, Southern France, and Italy. The beet thrives best in countries where a hot summer is followed by sudden and great cold, in such places it is biennial and accumulates a supply of sugar for its future needs. Mild damp climates, with many wind currents from the sea are unfavourable.

The author believes that the excellence of the roots grown in Bohemia, Poland, and Russia is due rather to these conditions of climate than to care in cultivation.

J. F.

**Quantities of Amides and Albuminoids in Green Plants: Decomposition of Nitric Acid and Ammonia in Plants.** By O. KELLNER (*Chem. Centr.*, 1879, 744—749; 761—768).—The author's results, which are arranged in the following table, show that green plants contain notable quantities of nitrogen in the form of amido-acids and acid amides.

The original paper contains a discussion of these results from the point of view of physiological botany.

Experiments are also detailed which show that peas grown in sand soaked with calcium nitrate, ammonium chloride, and ammonium nitrate respectively, and watered with solution of the same salts, contained from 5 to 7 per cent. of their total nitrogen in the form of amido-acids and acid amides, and about 2·5 per cent. in the form of albuminoid compounds.

|                                   | Total<br>nitrogen<br>per cent. | Nitrogen not present<br>as albuminoids. |  | Nitrogen<br>as amido-<br>compounds.<br>Per cent. |
|-----------------------------------|--------------------------------|---|--|--|
|                                   |                                | Per cent.                               | Calculated<br>in percents<br>of total<br>nitrogen. |  |
| <i>Lucerne.</i>                   |                                |   |  |  |
| 4 cm. high, 2 leaves .....        | 6·922                          | 2·133                                   | 30·5   | —  |
| 12     "     4     " .....        | 5·760                          | 2·042                                   | 35·5   | —  |
| Same, before flowering .....      | 3·570                          | 1·183                                   | 33·1   | 1·025  |
| 50 cm. high before flowering...   | 2·474                          | 0·721                                   | 29·1   | 0·613  |
| 50—60 cm. high, in flower....     | 3·008                          | 0·729                                   | 24·2   | 0·687  |
| <i>Red Clover in Second Year.</i> |                                |   |  |  |
| 4 cm. high, 3 leaves.....         | 5·200                          | 1·958                                   | 37·7   | —  |
| 7     "     6     " .....         | 3·974                          | 0·975                                   | 24·5   | —  |
| 35     "     full bloom .....     | 2·244                          | —                                       | 16·5   | 0·370  |

|                                 | Total<br>nitrogen<br>per cent. | Nitrogen not present<br>as albuminoids. |  | Nitrogen<br>as amide-<br>compounds.<br>Per cent. |
|---------------------------------|--------------------------------|---|--|--|
|                                 |                                | Per cent.                               | Calculated<br>in percents<br>of total<br>nitrogen. |  |
| <i>Espareet.</i>                |                                |   |  |  |
| 4 cm. high, 4 leaves . . . . .  | 3.028                          | 0.811                                   | 26.7   | —  |
| 8    "    9    "    . . . . .   | 3.251                          | 0.857                                   | 26.4   | —  |
| <i>Rye.</i>                     |                                |   |  |  |
| 8 cm. high, no internodes . . . | 4.433                          | 1.701                                   | 38.5   | 1.245  |
| 35   "    8    "    . . . . .   | 3.574                          | 0.901                                   | 25.2   | 9.758  |
| <i>Avena elatior.</i>           |                                |   |  |  |
| 17 cm. high . . . . .           | 4.644                          | 1.460                                   | 31.3   | —  |
| 55   "    seeding . . . . .     | 2.420                          | 0.637                                   | 26.3   | —  |
| <i>Dactylis glomerata.</i>      |                                |   |  |  |
| 15 cm. high. . . . .            | 5.091                          | 1.806                                   | 26.8   | —  |
| 45   "    seeding . . . . .     | 2.533                          | 0.452                                   | 17.8   | —  |
| <i>Meadow Plants.</i>           |                                |   |  |  |
| 1st cutting. . . . .            | 4.01                           | 0.875                                   | 22.8   | 0.763  |
| 2nd   "    . . . . .            | 2.61                           | 0.496                                   | 19.0   | 0.415  |
| 3rd   "    . . . . .            | 2.14                           | 0.293                                   | 13.7   | 0.257  |
| 1st   "    . . . . .            | 2.824                          | 0.983                                   | 34.8   | 0.892  |
| 2nd   "    . . . . .            | 1.787                          | 0.285                                   | 16.0   | 0.239  |
| 3rd   "    . . . . .            | 2.354                          | 0.102                                   | 7.5  | 0.033  |
| Meadow hay . . . . .            | 1.736                          | 0.218                                   | 12.6   | 0.175  |
| "    over ripe . . . . .        | 1.450                          | 0.233                                   | 16.1   | 0.187  |
| After hay . . . . .             | 2.269                          | —                                       | 15.0   | 0.349  |
| "    . . . . .                  | 2.384                          | —                                       | 15.0   | 0.356  |

M. M. P. M.

**Tannin of Sumach Leaves.** By H. MACAGNO (*Chem. News*, 41, 63).

|                      | Water.          |                 | Tannin.         |                 | Means. |         |
|----------------------|-----------------|-----------------|-----------------|-----------------|--------|---------|
|                      | Upper<br>sides. | Under<br>sides. | Upper<br>sides. | Under<br>sides. | Water. | Tannin. |
| June 10th, 1879..... | 58.15           | 60.23           | 24.93           | 17.45           | 59.19  | 21.19   |
| " 16th " .....       | 57.12           | 63.40           | 24.92           | 16.11           | 60.30  | 20.51   |
| " 27th " .....       | 52.47           | 63.44           | 25.82           | 15.27           | 57.95  | 20.54   |
| July 14th " .....    | 51.15           | 62.24           | 24.75           | 10.81           | 56.69  | 17.78   |
| " 29th " .....       | 49.80           | 60.83           | 23.80           | 9.44            | 55.06  | 16.62   |
| Aug. 11th " .....    | 48.15           | 61.80           | 21.91           | 8.77            | 54.97  | 15.34   |

The leaves were taken at the dates given from the upper and under sides of the branches respectively.

The larger quantity of tannin in the leaves from the upper side of branches is noteworthy.

M. M. P. M.

**Oxalic Acid in Beet Leaves.** By A. MÜLLER (*Bied. Centr.*, 1880, 236).—The results of the author's investigations show that the fresh leaves of the sugar-beet contain 4 per cent oxalic acid, of which one-third is in a soluble form. When it is considered how great are the quantities of these leaves eaten by cattle in countries where the beetroot sugar industry is large, it behoves farmers to be on their guard, as the acid induces inflammation of the mucous coats of the stomach. The pickling of the leaves with chalk is likely to prevent this unpleasantness, the soluble acid being converted into calcium oxalate, which is insoluble in the weak acids of the stomach.

J. F.

**Distribution of Potassium Nitrate in the Beet.** By H. PELLET (*Bied. Centr.*, 1880, 235).—The roots experimented on were grown in ridges after Champonnois' system. They were manured with 40,000 kilos. of stable manure and 1,200 kilos. of chemical manure per hectare; 80 cm. between the ridges, and 10–11 cm. between each plant in the row. The following is the amount of potassium nitrate:—

|                                  | Fresh substance. | Dry substance. |
|----------------------------------|------------------|----------------|
| Stalk and leaf-ribs . . . . .    | 0.846            | 8.46           |
| Green matter of leaves . . . . . | 0.148            | 1.10           |

Under normal conditions the roots contain less than the leaves, but when the whole contents are under the average, the root proportion is comparatively higher; for example, the author found in one plant fresh leaves, 0.76; roots, 0.48, whilst Pagnoul in others found in the leaves 0.006 and 0.292; in the roots of the same plant 0.008 and 0.193. The leaves which had fallen from a plant on 26th September were rich in the salt, equal to 1 per cent. at the time of their falling off.

The amount of the salt varies also in different parts of the root, one of 600 grams containing 11.58 per cent. sugar in the juice, gave in the middle 0.23, in the crown 0.80, and in the point 0.178 per cent. of potassium nitrate, the sugar in the point was 3 per cent. more than in the crown.

J. F.

**Effect of Cold on Cherry Laurel.** By FLÜCKIGER (*Pharm. J. Trans.* [3], 10, 749).—Cherry laurel leaves when exposed to intense cold, yield a small quantity of an essential oil differing from that obtained from the living plant. The oil has an acid reaction, but no traces of hydrocyanic, benzoic, or formic acid were found. The cause of the acid reaction is not known. Crystals separate out from the oil on standing (m. p. 60°).

L. T. O'S.

**Nutritive Value of Fruits.** By J. KÖNIG (*Bied. Centr.*, 1880, 239–240).—The following is a valuable contribution to our know-



ledge of the subject. An analysis of potatoes is added for the sake of comparison :—

|        |            | Soluble in water. |        |            |          |                  | Insoluble. |      |
|--------|------------|-------------------|--------|------------|----------|------------------|------------|------|
|        |            | Water.            | Sugar. | Free acid. | Albumin. | Protein and ash. | Seed husk. | Ash. |
| Apples | Minimum .  | 81.29             | 5.49   | 0.39       | 0.19     | —                | 1.37       | 0.17 |
|        | Maximum .  | 87.31             | 10.36  | 1.64       | 0.50     | —                | 3.46       | 0.46 |
|        | Average... | 83.58             | 7.73   | 0.84       | 0.39     | 5.17             | 1.98       | 0.31 |
| Pears  | Minimum .  | 80.00             | 6.58   | trace      | 0.21     | —                | 3.52       | 0.20 |
|        | Maximum .  | 86.00             | 11.52  | 0.58       | 0.50     | —                | 5.12       | 0.38 |
|        | Average... | 83.08             | 8.26   | 0.20       | 0.36     | 3.54             | 4.30       | 0.31 |
| Plums. | Average... | 81.18             | 6.15   | 0.85       | 0.78     | 4.92             | 5.41       | 0.71 |

|          |              | Water. | Nitro-<br>genous<br>substances. | Oil. | Non-nitro-<br>genous<br>extract. | Cellulose. |
|----------|--------------|--------|---------------------------------|------|----------------------------------|------------|
| Potatoes | Minimum ...  | 68.29  | 0.50                            | 0.05 | 12.05                            | 0.27       |
|          | Maximum...   | 82.88  | 3.60                            | 0.80 | 26.57                            | 1.40       |
|          | Average..... | 75.77  | 1.79                            | 0.16 | 20.56                            | 0.75       |

J. F.

**Influence of Steaming on the Digestibility of Hay.** By HORNBERGER (*Landw. Versuchs.-Stat.*, 24, 380—381).—These experiments on feeding oxen with steamed hay have as yet yielded no favourable result, the nitrogenous constituents of the steamed hay being present in a less digestible form than in ordinary dry hay: only 68 per cent. of the digestible nitrogenous constituents were assimilated (comp. this vol., p. 498).

J. K. C.

**Beet Residues as Fodder.** By H. PELLET and CH. DE LEVANDIER (*Bied. Centr.*, 1880, 280—284).—It is stated that the residue obtained by the diffusion method of extracting the juice from beetroots is of more value as a cattle fodder than either the residue obtained by hydraulic pressure or by maceration. Analyses are given, and a method is described for the proper preservation of the residues.

A. J. C.

**Damage to Seed Peas by Weevil.** By G. MARCK (*Bied. Centr.*, 1880, 201—203).—There are different opinions as to the value of peas which have suffered from the attacks of this pest; it is admitted that they are unsuited for human food, but many persons think they can be used as seed. To settle the question, the author examined two sorts, which out of 13 grown for experimental purposes, were found to be considerably damaged. Of every 100 seeds it was found that 40 on an average were injured. 100 sound peas weighed 21.20 grams, the

same number of damaged only 16.30, or a difference of 23.1 per cent. Of 100 of the partially eaten peas 74 had the radicle and plumula both seriously damaged, and in 13 only were neither injured. In the majority of cases the portion of seed which is considered the most valuable, suffered. A chemical analysis given in the paper verifies this observation, and the author gives as his opinion that damaged peas should not be used as seed. The prevention of the damage next engaged the author's attention. The effect of a high temperature and of chemicals in particular, was tried. The employment of heat is not always possible; malt kilns must be used, and they shrivel and dry up the seed, make it look old and unsightly, and there is a danger of killing it by careless manipulation. The employment of chemical solutions has the advantage of killing the worm without the destruction of the seed, but is still injurious. The seeds swell up, and unless they are sown at once, they must be spread out and dried; they become wrinkled, and lose their marketable appearance. Large space is required, and in unfavourable weather considerable loss is sustained by mildew. Another plan proposed is to leave the seeds over for a second year, which certainly frees them from live insects, but then the damage done is far greater. Amongst gaseous remedies carbon bisulphide vapour is the best and cheapest, others, such as alcohol and ether vapour, being effectual, but dangerous and expensive.

J. F.

**Symphytum aspernum** as a Fodder. By E. WILDT and others (*Bied. Centr.*, 1880, 290—298).—This plant, which belongs to the family *Boraginæ*, is shown to be of great value as a cattle fodder, and as it grows rapidly and gives a large produce, it would repay extensive cultivation. Wildt's analysis of the dried plant gave per cent.: protein substances, 22.37; fibre, 13.24; fat, 3.06; non-nitrogenous extractive matter, 43.04; ash, 18.29; phosphoric acid, 1.62; potash, 7.87; lime, 3.74. A previous analysis by Voelcker showed 23.37 per cent. protein substance in the leaves, and 13.06 in the stem; non-nitrogenous matter, 54.49 and 72.49; ash, 17.74 and 14.45 in the leaves and stem respectively. Its properties and the method followed in its cultivation, are also described.

A. J. C.

**Chemical Examination of Ligneous Papilionaceæ.** By P. FLICHE and L. GRANDEAU (*Bied. Centr.*, 1880, 284—286).—Four species growing on a siliceous soil were examined, viz., *Cytisus Laburnum*, *Ulex Europæus*, *Sarothamnus vulgaris*, and *Robinia Pseudo-acacia*. The results indicate that plants of the same natural family growing on the same soil differ considerably in the amount and in the distribution of starch and in the amount of ash and nitrogen. The percentage composition of the ash shows still greater variation. These differences increase or decrease according as the relationship between the plants becomes more or less distant. The soil is exhausted in an unequal degree by different members of the same family.

Comparison is made between the mineral constituents which were absorbed from the soil by each of the four kinds, not one of which would repay cultivation.

A. J. C.

**Cultivation of Sugar-Beet.** By A. LADUREAU (*Bied. Centr.*, 1880, 286—288) and H. CHAMPONNOIS (*ibid.*, 288—289).—The authors have independently examined the two methods which are generally employed in the cultivation of the sugar-beet, but the results obtained are somewhat contradictory as to whether ridge culture is the more advantageous. A. J. C.

**Cultivation of the Yellow Lupine.** By E. WEIN (*Bied. Centr.*, 1880, 261—265).—A confirmation for the most part of Lehmann's results (this Journal, 1876, 1, 734), that this plant is able to thrive in soils which are not supplied with nitrogenous manure, and that the nitrogen when supplied should be in the form of nitrate (of soda). Instead of fallowing the soil, it is stated that the same result may be obtained with greater profit by cultivating the lupine. A. J. C.

**Fallowing.** By E. WOLLNY (*Bied. Centr.*, 1880, 252—258).—The author has examined the influence of fallowing on (a) the temperature, (b) on the humidity, and (c) on the decomposition of the soil.

a. A soil in fallow is warmer in summer, but colder in winter, whilst the variations in the temperature are considerably greater than is the case in a soil which is covered with a plant surface.

Plants prevent the direct action of the sun's rays on the surface of the soil, and consume a quantity of heat, which is thus lost to the soil, in the process of transpiration and of nocturnal radiation. Moreover, as the upper organs of perennial plants decay, they form a surface cover to the soil, and in this way the cooling action of the air and of radiation is diminished. On fallow land the reverse action occurs; there is unimpeded radiation, and the temperature of the surrounding air is communicated to the surface of the soil and thence transmitted to a lower stratum.

b. The amount of water in a cultivated soil in vegetation is always less than is in the same land in a state of fallow. This law is good for all kinds of soils in fallow, even after repeated harrowing, &c. The reasons that are given in explanation of this rule are in accordance with those which have been previously stated by the author (this Journal, Abst., 1880, 498).

Experiments on grass and clover land and on quartz-sand, turf, and clayey soils, show that with the same rainfall a considerably larger quantity of water percolates through a soil in fallow than through a soil which is covered with a vegetating plant surface.

It is therefore apparent that fallowing plays an important part in regulating the humidity of the soil, and in sustaining the crops in seasons of drought. It also partly accounts for the favourable results obtained by growing rape after a crop of close growing and desiccating plants, such as clover and clover grass, especially if the land has been harrowed and kept in fallow some time previously to sowing out,—and of wheat after rape. In the latter case the soil has had time in the interval—July to September—to re-absorb an amount of moisture equal to that withdrawn from it by the previous crop.

c. The generally humid condition of fallow land, together with a higher temperature, promotes the decomposition of humus substances,

and enriches the air of the soil in carbonic anhydride. It was found by Pettenkofer's method that the amount of carbonic anhydride in the air in the soil at a depth of 25 cm. on land in fallow was on an average during May to November, four times as great as that in grass land.

This excess in carbonic anhydride is favourable to the decomposition of the insoluble constituents of the soil, thus increasing the nutritive value of the soil to plant-life. Whilst as a general rule it may be stated that fallowing is advantageous to the soil, yet under some conditions it may have the contrary effect. It is injurious for instance on sandy soils, where the object should be to keep the soil as much as possible under a plant surface in order to avoid a washing out of its soluble constituents; also on clayey soils in damp climates or with much rainfall, as the excess of water being unable to drain off by percolation lies on the surface of the land. Winter fallowing on binding soils is of value in assisting the disintegration of the soil by a successive freezing and thawing of the enclosed particles of water; in this way the soil acquires a structure which could be given to it only by a considerable expenditure of labour. A. J. C.

**Behaviour of Natural Soils and of Plants Growing in them towards Water.** By G. HAVENSTEIN (*Bied. Centr.*, 1880, 244—252).

**Absorption of Ammonia by the Soil.** By ORTH (*Landw. Versuchs.-Stat.*, 24, 376—379).—The absorption of ammonia by the soil varies with the quantity of oxide of iron or humus present. If sandy soils be mixed with loam or moor soil, the absorption of nitrogen is proportionately increased, especially by the latter. J. K. C.

**Influence of Forests on the Rainfall.** By M. FAUTRAT (*Bied. Centr.*, 1880, 241—244).—Forests, and pine forests more especially, have the property of attracting aqueous vapour, so that the rainfall is greater over a pine forest than over a contiguous area which is unplanted. This conclusion is supported by the results of the hygro-metric and rainfall determinations which were obtained in the two cases, under similar conditions as regards elevation. A. J. C.

**Comparative Rainfall in Woods and Fields.** By A. MATTHIEU (*Bied. Centr.*, 1880, 164—168).—This paper is an abstract of a report made by the President of the Administration of Forests in France, on certain meteorological observations made during eleven years at the three stations in the neighbourhood of Nancy, two of them situated in the forest, and one in the open country, their object being to determine, 1st, the effect of wooded and open land on the quantity of water absorbed by the soil; 2nd, the proportion according to which the leaves hinder the rain reaching the soil; 3rd, the evaporation on wooded and on open ground; 4th, the temperature of the air within and without the wood. The averages of the eleven years' rainfall at the two forest stations were as 100 and 97, and at the open station 81, from which it would appear that the influence of forests is to increase the rainfall, and that therefore forests are useful in feeding springs and streams.

but these observations, taken in a limited district, are not accepted by the author as conclusive without further consideration.

The amount of rain which reached the soil under the trees was quite as much, indeed rather more than in the open ground.

The amount of evaporation varies with the temperature in the open ground, but in the woods it remains tolerably constant; the total evaporation in the former was in the eleven years three times as great as in the latter.

The temperature within the forest on an average of nine years was half a degree Cent. below that of the open ground, but the variations less in amount. J. F.

**Injurious Effect of Peat Water on Meadows.** By KLEIN (*Bied. Centr.*, 1880, 168—171).—This paper was called forth by an overflow of black bog water in a certain district of East Prussia, and the investigations which were then made as to the amount of damage caused by the overflow. The Royal Commissioner collected a quantity of the water, and sent some to different experimental stations, with a request for analysis and experiment. It was found that the water contained in solution 31.28 per 100,000 organic matter (humic acid); 17.59 mineral matter, lime, iron, &c., together with a very large proportion of suspended matter, humic and geic salts, and finely divided particles of humus, the organic matters being presumably those injurious to vegetation, firstly, by giving opportunity for the formation of the so-called bog stone or bog ore, and thereby diminishing the space available for the roots of plants, and also by acting as a reducing agent, and producing chemical combinations poisonous to vegetation.

When this water is taken from its collecting ground, where it has not had access to the oxygen of the air, its chemical composition undergoes alteration. Combinations of humus and iron dissolved in the water are precipitated, and gradually permeate the soil, becoming so intimately combined that hard stony masses are formed, which after a time experience further changes, rendering them fatal to vegetation; the surface of the earth becomes hard and impervious to the oxygen of the air, and the humus, withdrawing oxygen from the iron compound, forms salts destructive to vegetable life. Particularly unsuitable are such waters to clay with a marly subsoil, whilst strong calcareous soils bear it better, because of the property which lime possesses of decomposing humus. Upon meadows growing on the latter kind of soil the effect is most injurious, and might result in changing it to moorland. The result of the series of experiments is decidedly against the employment of this water in any farming operations. J. F.

**Manure Experiments with Rye, Wheat, and Oats.** By A. PAGEL and H. MEYER (*Bied. Centr.*, 1880, 178—182).—The reluctance of small farmers to employ artificial manures is considerable, except in the neighbourhood of large farms, where example leads to their partial use. The authors instituted the following experiments, believing that strong efforts should be made to overcome this reluctance.

The first experiment was to ascertain if it would pay better to employ a large or a small quantity of manure; four spaces of 140 square meters were carefully tilled and prepared exactly in the same way, one was manured with sheep's dung; the other with 600 kilos. of bone-meal; the third with 300 kilos. bone-meal; and the fourth, 400 kilos. superphosphate.

The tabulated results show that the employment of the large quantity of bone-meal yielded the largest crop, but the 300 kilos. plot paid the best interest on the capital expended.

The second experiment was to ascertain if the employment of larger or smaller quantities of superphosphate after the bone-meal of the preceding year, paid better interest on the capital employed; and at the same time trials were made as to whether sodium nitrate when used should be dug in or used as top dressing. The experiments prove to the authors' satisfaction that the use of 400 kilos. of superphosphate per hectare is more profitable than 200 kilos., and that the employment of sodium nitrate is more successful as top dressing than when dug in or sown with the seed; in the latter case a considerable amount of nitrogen is lost by sinking into the ground before the plants are ready to assimilate it.

The third series of experiments was made to verify the effects of artificial manures used with stable dung. The same course of treatment was pursued, and the conclusion arrived at was, that the use of the artificial manure increased the produce considerably. J. F.

**Bone-meal as a Manure for Potatoes.** By MEYER (*Bied. Centr.*, 1880, 265—268).—Bone-meal manure increases the weight of the produce, but it is uncertain whether its action is to increase the size or the number of the tubers. It probably tends to develop the entire plant. A. J. C.

**Report by Dr. Petermann "On the Agricultural Value of so-called 'Retrograde Phosphoric Acid,' and Discussion thereon, at the Meeting of Directors of Agricultural Experimental Stations, held at Karlsruhe, September 16 and 17, 1879.** (*Landw. Versuchs.-Stat.*, 24, 310—358.)—It is the universal opinion of French chemists, that the agricultural value of retrograde phosphoric acid is equal in all respects to that of the soluble form; accordingly, in analyses of superphosphate conducted in France, the worth of the article is fixed by the sum of soluble and retrograde phosphoric acid, the latter being estimated by means of its solubility in citrate of ammonia. Experiments by Grandeau, Koeth, and others point to this conclusion, which, however, has, up to the present time, not been accepted by German chemists. The author has therefore performed some experiments, with the view of ascertaining the relative values of soluble and retrograde phosphoric acid in the most effective manner possible. The plants made use of in his experiments were peas and barley; these were grown in pots containing known quantities of soil and manure, the latter consisting of soluble or retrograde phosphoric acid, precipitated dicalcium phosphate, soluble in ammo-

nium citrate, or rendered insoluble by heat. The following table gives the results of the experiments:—

### I. Peas.

|   | Fruit.<br>Grains. | Straw and<br>pods.<br>Grains. | Total.<br>Grains. |
|---|-------------------|-------------------------------|-------------------|
| Pots I and II, without manure.....                  | 46·24             | 28·79                         | 75·03             |
| „ III and IV, soluble phosphoric acid               | 50·48             | 34·52                         | 85·00             |
| „ V and VI, retrograde phosphoric acid.....         | 49·58             | 33·70                         | 83·28             |
| „ VII and VIII, precipitated phosphate .....        | 54·20             | 32·00                         | 86·20             |
| „ IX and X, precipitated and heated phosphate ..... | 47·11             | 27·97                         | 75·05             |

### II. Barley.

|                 |                 | Grains. | Straw and<br>chaff.<br>Grains. | Total.<br>Grains. |
|-----------------|-----------------|---------|--------------------------------|-------------------|
| Pots I and II.  | As before ..... | 20·66   | 45·32                          | 65·98             |
| „ III and IV.   | „ .....         | 25·32   | 50·60                          | 75·92             |
| „ V and VI.     | „ .....         | 23·98   | 48·98                          | 72·96             |
| „ VII and VIII. | „ .....         | 27·31   | 56·21                          | 83·52             |
| „ IX and X.     | „ .....         | 21·83   | 46·45                          | 68·28             |

From the above results we see that in the case of the peas, retrograde phosphoric acid produced as great an increase of yield as the soluble form, and that in the case of both peas and barley, precipitated phosphate produced a greater yield than either, whereas phosphate, insoluble in ammonium citrate, had hardly any effect. These experiments then confirm the conclusion previously arrived at by the author, that phosphate soluble in ammonium citrate is to be regarded as of equal value with phosphate soluble in water. In the case, indeed, of soils poor in lime, it is even more advantageous to use precipitated than soluble phosphate, as Völcker's experiments show.

The author employs a combination of Joule's and Fresenius' methods for the estimation of the retrograde phosphoric acid.

Dr. Fleischer communicated the results of experiments with phosphates in various conditions on moorland; in the majority of cases, retrograde and insoluble phosphoric acid produced greater yields than the soluble form, the reason of this lying in the poor absorptive power of such soils. He also deprecated the drawing of conclusions from isolated experiments.

H. Albert gave an account of some experiments carried out by himself, in conjunction with Volbrecht, on the absorption of soluble and insoluble phosphates by various kinds of soil. They found that when soluble phosphate was introduced into sandy soil poor in lime, a quick distribution of the phosphoric acid took place, so much so that the greater part of it was soon out of reach of the plant; in the case of dicalcium phosphate this did not take place, and the effect of the phos-

phoric acid was visible for two or three years afterwards, the dicalcium phosphate becoming gradually insoluble in ammonium citrate.

After a somewhat lengthy discussion, a motion was carried to the effect that while recognising the value of retrograde and precipitated phosphoric acid when applied to certain kinds of soil, the meeting does not consider the evidence laid before it as conclusive in establishing the relative agricultural value of retrograde in contradistinction to soluble phosphoric acid.

J. K. C.

**Nitrogen Manure for Oats.** By E. HEIDEN (*Bied. Centr.*, 1880, 259—261).—Nitrogen in the form of nitrate—50—100 kilos. of Chili saltpetre per hectare as a top manure—is more efficacious for oats than in the form of ammonia.

A. J. C.

**Chili Saltpetre for Beets.** By PLUCHET (*Bied. Centr.*, 1880, 259).

**Manuring Beets with Sodium Nitrate.** By M. MÄCKER (*Bied. Centr.*, 1880, 175—178).—A field was divided into six portions, the seed and manure employed were, as far as possible, of the same quality, and evenly divided. The ground was prepared exactly the same in each portion: plots No. 2 and 5 had no manure, No. 1 received 25 kilos., No. 3 50 kilos., No. 4 75 kilos., No. 6 100 kilos. of sodium nitrate. 50 kilos. of seed in No. 1 produced 456·60 of roots; No. 3 580·50; No. 4 600·87; No. 6 610·05.

A second series of experiments was made under similar conditions for the purpose of comparing the amount of sugar in beets grown with superphosphate and with sodium nitrate; the results were unfavourable to the nitrate, but not conclusive, and further investigations are invited. The author dwells on the importance of an extended series of such experiments, the great development of the beet-sugar industry having caused the exhaustion of the soil in many localities, so that a strongly nitrogenous manure is required.

Sodium nitrate fulfils many of the necessary conditions, but it has not yet been decided whether it is advantageous or not to use it.

J. F.

**Thirty-eighth Year of a Farm without Stable Manure.** By SPECHER (*Bied. Centr.*, 1880, 172—175).—This is the third decennial report of the farm of Wingendorf, conducted by the author since 1840 on the principle of keeping no cattle and not using any stable manure. Since last report the property had passed into the hands of the Government, which on the representation of the leading agriculturists of the district, continued the experiment, under the care of the author, and it was made auxiliary to the State farm of Bräunsdorf for purposes of comparison; the latter farm was considered very fertile. This arrangement allowed the author to compare results very closely, as the two farms were treated exactly alike except in the matter of the manure.

In the five years, 1873—1877, the rye crop at Wingendorf exceeded that at Bräunsdorf by an average of 46½ kilos. per hectare, and the oats 11½ kilos. per hectare; the straw being as abundant in one as in



the other. Potatoes were not so successful, showing a deficiency of 46·47 hectolitres per hectare, whilst clover and flax have failed for many years, on which account a longer interval between the cultivation of these crops has been decided on.

The climate, soil, and situation of the two stations are very similar, yet at Wingendorf the crops of clover yielded scarcely 20 per cent. of a full crop: the grasses sown with the clover suffered equally; the seeds germinated well enough, and promised a good crop in April, but in May and June they failed.

An examination of the manures put on the farm showed that in the ten years from 1858—1867, there were 7786·55 kilos., and from 1868—1877 3580·57 kilos. more phosphoric acid put into the ground than was taken out of it. The large quantity of this class of manure was proved to have been unnecessary by the results of the last ten years, when the yield was so satisfactory without further additions of phosphates.

During the first ten years 2861·25 kilos., and in the last 943·3 kilos., more nitrogen was removed from the soil than had been added. The author considers the excess was in part drawn from the atmosphere. Of potash salts in both periods considerably more was taken off the farm, respectively, 4641·5 kilos. and 3837·5 kilos. than had been added to it. Analysis showed, however, that the soil was very rich in potassium. To secure its solubility a large quantity of lime manure was required, which was very liberally used, the first ten years showing an excess of 13,658·9 kilos., the second ten years 7898·35 kilos. over and above the quantity of lime taken off the farm.

What has been the cause of the failure of the clover, what properties are possessed by the stable manure, which is absent from the phosphoric, nitrogenous, potash, and lime manures, the author cannot explain, the condition and treatment of both farms being so exactly similar that no practical farmer could discern any difference; the only explanation that can be given being a supposition that the farm has been attacked with the clover sickness, which sometimes attends clover fields where this crop is grown for the sake of seed only. J. F.

**Beet-sugar Refuse as Manure.** By E. v. WOLFF (*Bied. Centr.*, 1880, 171—172).—In the process of clarifying the syrup from the sugar-beet with lime large quantities of slime separate; it has frequently been submitted to analysis, in order to determine its value for manurial purposes; it contains varying amounts of moisture, and about 1—2 per cent. phosphoric acid, with perhaps  $\frac{1}{4}$  of a per cent. of nitrogen; its principal value, however, is the lime, which is useful by bringing into play the vegetable matters in the soil in the form of humus, and also when the soil is inclined to be of a sour nature. The phosphoric acid is about four times, and the nitrogen scarcely half as much as in ordinary stable manure. The employment of this material is only to be recommended in conjunction with stable manure in about equal proportions; it is a valuable ingredient in a compost; its money value being altogether dependent on the cost of carriage and similar commercial considerations. J. F.

## Analytical Chemistry.

**Modification of V. Meyer's Vapour-density Apparatus.** By J. PICCARD (*Ber.*, 13, 1079—1080).—The object of this modification of Meyer's vapour-density apparatus is to avoid the error due to the replacing of the cork after the tube containing the weighed quantity of substance has been dropped in. For this purpose the headpiece, above the evolution-tube, is so arranged that it may be bent down at right angles, which is attained by having it in a separate piece, and attached to the rest of the apparatus by a moveable joint of india-rubber. In an actual experiment the headpiece is brought down to the horizontal position, the tube containing the substance pushed into a short distance, and the cork replaced. The apparatus is maintained in this position till no more bubbles issue from the evolution-tube, showing that the temperature is constant. When this is the case the headpiece is brought back to the vertical, and the tube containing the substance slides down into the bulb of the apparatus, and is there converted into vapour. T. C.

**New Form of Instrument for the Determination of Specific Gravity.** By F. P. DUNNINGTON (*Chem. News*, 41, 154—155). This instrument may be described as a Nicholson's hydrometer, with a thick graduated stem, the graduations on the stem being in one-tenth c.c. Instead of the upper pan of the Nicholson there is a graduated tube for holding water or other liquid and the solid under examination. The weight of the solid or liquid under examination is obtained from the increase of volume of water displaced by the stem on placing the substance in the upper tube. The volume of the substance if solid is obtained from its displacement in the upper tube, or if liquid is read directly. F. L. T.

**New Method of taking the Specific Gravity of Liquids.** By H. SOMMERKORN (*Chem. News*, 41, 203).—The apparatus required is a thin-sided glass tube, divided into millimeters, and of from 3—4 centimeters in diameter, and a thin circular plate of exactly the same diameter held by a string. The tube is closed with the plate, and the apparatus plunged into the liquid to be examined, pulling the plate against the tube with the string. If it is plunged deep enough the pressure causes the plate to adhere; on slowly raising it in a vertical direction, the point is easily observed at which the plate, after merely hovering, sinks. The depth of the tube in the liquid is now read off.

$$\text{Sp. gr.} = \frac{\text{Weight of glass plate}}{\text{Area of glass plate} \times \text{depth of tube in liquid}}$$

The weight and area being constant, the depth is the only variable quantity. F. L. T.

**Detection of Hydrochloric Acid by Sulphuric Acid and Potassium Dichromate.** By H. W. WILEY (*Chem. News*, 41, 176—177).—Instead of distilling the mixture of the chromate, sulphuric acid, and suspected chloride in a retort, they are distilled from a beaker, and the chlorochromic anhydride is condensed on the under surface of another beaker suspended inside the first, and containing ice or ice and salt. A stirring-rod moistened with the chlorochromic anhydride is brought into contact with a drop of sulphuric acid and a crystal of strychnine, the colour test for strychnine being readily produced.

In many cases the author has not succeeded in obtaining any chlorochromic anhydride when operating on mixtures of iodides and chlorides.  
F. L. T.

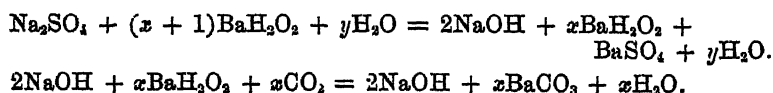
**Determination of Active Oxygen in Barium or Hydrogen Peroxide.** By M. A. BERTRAND (*Chem. News*, 41, 215).—Known quantities of either substance are added to pure hydrochloric acid (free from uncombined chlorine), excess of potassium iodide (free from iodate) added, and the liberated iodine, after the addition of an excess of hydrogen sodium carbonate, is titrated by thiosulphate.

F. L. T.

**Estimation of Sulphur in Pyrites.** By B. DEUTECOM (*Zeits. Anal. Chem.*, 1880, 313).—Estimation of sulphur in pyrites by oxidation with nitric acid and precipitation as barium sulphate gives unsatisfactory results. The author recommends fusing 1 gram of the pyrites with 8 grams of a mixture of equal parts of potassium chlorate, sodium carbonate, and sodium chloride, in a large covered porcelain crucible. When cold the mass is extracted with water, and the sulphuric acid estimated in the solution. The residue is quite free from sulphur.

A. J. G.

**Alkalimetric Determination of Sulphates.** By J. GROSSMANN (*Chem. News*, 41, 114).—The process is based on the following reactions:—



At present the author has applied the process only to the determination of sodium sulphate in salt cake. The sample is dissolved in water; excess of a cold saturated solution of baryta is added; the whole is made up to a determinate volume and filtered; carbonic anhydride is passed through an aliquot portion of the filtrate; the liquid holding the precipitated barium carbonate in suspension is boiled, allowed to cool, made up to a fixed volume, and filtered; and alkali is determined in an aliquot portion by one-fourth normal acid.

The chief sources of error are:—(1) Presence of barium nitrate in the baryta used; this converts some of the sodium sulphate into nitrate, and therefore diminishes the amount of alkali found in the last operation. If the solution of baryta be precipitated by carbonic

anhydride, and the barium remaining in solution after filtration be determined, an estimation is arrived at of the amount of barium nitrate in the specimen of baryta used.

(2) Errors of measuring vessels. The original contains an account of a modification of Gavolovski's method (*Chem. Centr.*, 1879, 236) for correcting this error.

(3) Error due to the bulk of the precipitate in the measuring flasks. Experiments must be made with the flasks, liquids, &c., employed by each analyst for the determination of the magnitude of this error. In the author's determinations it was equal to about 0.4 per cent. in the first result.

(4) Certain unavoidable losses. The author states these are about equal to 1.3 per cent. As yet he has been unable to find the cause of those losses.

M. M. P. M.

**Separation of Silicic Anhydride in the Analysis of Limestones, Iron Ores, and other Minerals.** By H. ROCHOLL (*Chem. News*, 41, 234—235).—In the examination of many minerals for silicic anhydride by evaporating to dryness with hydrochloric acid and extracting with hydrochloric acid and water the insoluble residue is found to consist not only of silicic anhydride, but also of aluminium silicate. This necessitates either fusion of the insoluble residue with alkaline carbonates or in the absence of iron and certain rarer bodies; if absolute accuracy is not required it may be treated with hydrofluoric and sulphuric acids and ignited and the difference assumed to be silicic anhydride, the residue being aluminium oxide. To avoid this the author, if the mineral is of a basic character, ignites it previously to acting on it with hydrochloric acid, when he finds the insoluble residue to be pure silicic anhydride. In the case of iron ores the sample, after ignition has to be re-weighed and re-powdered, allowance of course being made for loss on ignition: when the ore contains more than 25 per cent. silicic anhydride it is necessary to add some ferric oxide before ignition to insure accurate results.

The residue may still contain barium sulphate and titanous anhydride. In the former case, after treatment with hydrofluoric and sulphuric acids and ignition, the loss is taken as silicic anhydride; in the latter case the titanous anhydride may be separated by known methods.

F. L. T.

**Estimation of Nitrous Compounds in Manufacture of Sulphuric Acid.** By J. MACTEAR (*Chem. News*, 41, 16, 43, 52, and 67).—The author describes a process for estimating "total acids" in the gases aspirated from the leaden chambers and from the Gay-Lussac towers. The gases are passed into a series of four tubes, three of which contain standard soda-solution and the fourth water coloured by litmus: bleaching of this litmus indicates escape of sulphurous or nitrous acid. After aspiration of a measured volume of gases, the residual alkali in the tubes is determined by standard acid, the liquid is then diluted and sulphuric acid is determined in an aliquot portion. The results are checked by a determination of the amount of ammonia evolved from a portion of the liquid by which the gases have

been absorbed by the action of zinc and iron in presence of caustic soda.

Details of the method adopted for the ammonia determinations are given. Heating must be continued until the contents of the vessels become pasty; alkali is sometimes carried over, it is therefore well, after titrating the distillate, to add a known excess of standard soda; boil until all ammonia is expelled, and titrate with standard acid.

The "permanganate method" is criticised. Experiments are described which show that "nitrous vitriol" may contain  $N_2O_5$ ,  $N_2O_3$ ,  $NO$ ,  $SO_2$ ,  $As_2O_3$ , and  $As_2O_5$ , and that therefore reduction of permanganate may be caused by substances other than nitrous compounds.

M. M. P. M.

**Direct Method of Testing Vitriol Exits for Nitrogen Compounds.** By G. E. DAVIS (*Chem. News*, 41, 188—189).—A known volume of the exit gases is drawn through a measured quantity of hydrogen peroxide and the necessary amount of water. The resulting solution is made up to a definite volume and divided into three portions. In one the total acidity is determined by pure sodium hydrate, it is then acidified, and the sulphuric acid determined as barium salt. In the second the hydrochloric acid is determined by a standard silver solution after decomposing the excess of peroxide by potassium permanganate and neutralisation. The third portion is treated with a little silver sulphate, neutralised, filtered, and evaporated on the water-bath to about 1 c.c. When cooled a drop or two of sulphuric acid is added to decompose carbonates, and the solution is then transferred to Crum's nitrogen tube. Twice its volume of pure and concentrated sulphuric acid is now added, and the whole shaken up with the mercury; the evolved nitric oxide is allowed to cool, and measured.

F. L. T.

**New Blowpipe Test for Phosphoric Acid.** By W. A. ROSS (*Chem. News*, 41, 187).—The test is based on the well-known property of pure tungstic acid to afford a bright blue bead in the reducing flame of the blowpipe with phosphor-salt, but only a yellowish or brownish bead with borax. The suspected phosphate is heated on a potash bead with potassium pyrotungstate in the *peroxidising pyrocone*, when a blue colour is produced. It has been suggested to the author that this blue is due to a trace of manganese in his tungstic acid, but he is of a different opinion.

F. L. T.

**Behaviour of Sulphuretted Hydrogen with Salts of the Heavy Metals.** By H. DELFFS (*Chem. News*, 41, 279).—As the limit between precipitable and non-precipitable metals is modified by the substitution of acetic for hydrochloric acid, so is it further modified by replacing acetic by formic acid. Zinc is precipitated, but cobalt, nickel, iron, and manganese are not precipitated in the last case. Manganese is not precipitated from propionic, butyric, and valerianic acid solutions. On adding to a mixture of cobalt and nickel nitrates, sodium acetate, insufficient for complete double decomposition, and treating with sulphuretted hydrogen, we obtain either cobalt free from nickel as a precipitate, or nickel free from cobalt in solution, according to the amount

of sodium acetate added. This is a very convenient method for obtaining either of these metals in a state of purity. F. L. T.

**Electrolytic Determination of Metals.** By L. SCHICHT (*Chem. News*, 41, 280).—Uranium, from alkaline solutions (containing tartaric, citric, or acetic acids, or mixed with sugar) or from neutral solutions, is separated only to a very small extent with a yellow colour; in presence of mineral acids it is not precipitated, but is reduced from uranic to uranous oxide.\*

Thallium is not precipitated from acid solutions, but is completely precipitated on the negative pole, with brisk disengagement of gas, from ammoniacal solutions, blackish-brown thallium oxide, much resembling lead peroxide, being deposited on positive pole; imperfectly precipitated from neutral solutions on account of the acid liberated. The oxide dissolves in hydrochloric acid with evolution of chlorine.

Indium is completely precipitated as metal at the negative pole, both from acid and alkaline solutions; in the latter case the metal is very bright and firm.

Vanadium. No precipitation, but merely reduction in alkaline or acid solutions.

Palladium nitrate, acidified with nitric acid, is deposited at the negative pole as bronze-coloured coating, which becomes darker and finally black. Some reddish oxide forms at positive pole. Alkaline solutions behave similarly, but the composition is slower and more adhesive.

Molybdenum, from an ammoniacal solution of molybdic anhydride, is completely and firmly deposited at the negative pole as molybdous oxide, as coloured rings which thicken and become black.

The first blue precipitate is molybdic molybdate, then follows molybdic and molybdous oxides. In acid solutions there is no precipitation; in ammonium molybdate acidified with molybdic anhydride, there is incomplete precipitation.

Selenium is completely thrown down both from acid and alkaline solutions. If the current be strong the deposit is pulverulent.

Tellurium behaves like selenium, but is deposited much more readily in acid solutions with a blue-black colour, in alkaline solutions in a very loose state at the positive pole, with strong disengagement of gas.

Gallium, like zinc, is thrown down completely at the negative pole in a pure state. F. L. T.

**Electrolytic Estimation of Silver.** By H. FRESSENIUS and F. BERGMANN (*Zeits. Anal. Chem.*, 1880, 324—327).—Luckow first proposed to estimate silver electrolytically (*Dingl. polyt. J.*, 178, 43; see also *Zeits. Anal. Chem.*, 1880, 1; this vol., 282). The authors have reinvestigated his process, and recommend the following method of procedure, the battery and electrodes being the same as mentioned in the Abstract. 200 c.c. of solution should be employed containing 0.03—0.04 gram of silver and 3—6 grams free nitric acid; the electrodes should be 1 c.m. apart, and the strength of current capable of evolving 150 c.c. of mixed gases from water per hour. The silver

\* This agrees with C. Luckow (this vol., 282).

separates in compact metallic form on the negative pole, no silver peroxide being deposited on the positive.

A. J. G.

**Estimation of Silver in Galena.** By C. BALLING (*Chem. News*, 41, 42). The ore (3—5 grams) is fused with 3 or 4 parts of a flux consisting of equal parts of soda and nitre. The mass is heated with water and filtered; the residue is evaporated to dryness with addition of nitric acid, and treated with very dilute nitric acid, and the solution is filtered; when the filtrate is cold, ferric sulphate is added and the silver determined by titration with ammonium thiocyanate.

M. M. P. M.

**Actual State of the Determination of Zinc.** By W. ALEXANDROWICZ (*Chem. News*, 41, 279).—In presence of sufficient acid, no appreciable quantity of zinc is precipitated by sulphuretted hydrogen from solutions containing copper or arsenic. For great exactness a double precipitation is recommended in pursuance of copper, although in such a case it is impossible to completely separate zinc and cadmium.

To separate iron and zinc, the mixture should be poured drop by drop into ammonia, not *vice versa*. The zinc remains in solution; the precipitate is washed with dilute ammonia.

To separate manganese and zinc, acidify with acetic acid, and precipitate by sulphuretted hydrogen. All the manganese remains in solution.

F. L. T.

**Estimation of Cadmium in Presence of Zinc: Separation of Zinc, Cadmium, and Copper.** By C. C. HUTCHINSON (*Phil. Mag.* [5], 8, 433—438).—The separation of cadmium from zinc in an acid solution by means of hydrogen sulphide is rarely complete, and the methods based respectively on the insolubility of hydrated cadmium oxide in a solution of an alkaline tartrate, and the solubility of zinc sulphide in solution of potassium cyanide, are also unsatisfactory. Accurate results may be obtained by the following method. The hydrochloric acid solution of the two metals is evaporated to dryness on a water-bath, the residue dissolved in water, and the solution, which should be moderately dilute, is heated to boiling, and sodium carbonate added in slight excess. After standing for some time the granular precipitate is filtered off, transferred to a platinum dish, and mixed with a considerable quantity of a saturated solution of ammonium sesquicarbonate. The mixture is well agitated, and left in a warm place for about 6 hours: the whole of the zinc carbonate is then dissolved. The insoluble cadmium carbonate is filtered off and converted into oxide. The filtrate is evaporated to small bulk to expel excess of ammonium carbonate, diluted, and the zinc is estimated by means of standard sodium sulphide solution. In the separation of copper, cadmium, and zinc, the most accurate results are obtained by precipitating the copper as cuprous thiocyanate, by means of potassium thiocyanate in presence of sulphurous acid. The zinc and cadmium in the filtrate may be separated by the preceding method.

C. H. B.

**Volumetric Determination of Cerium.** By F. STOLBA (*Chem. News*, 41, 81).—Cerium, when freed from lanthanum and didymium, may be precipitated as oxalate, and determined by means of permanganate solution. M. M. P. M.

**Estimation of Ferrous Iodide.** By R. H. PARKER (*Pharm. J. Trans.* [3], 10, 851—854).—The reaction which takes place between potassium chlorate and ferrous iodide may be used to determine the strength of a syrup of iodide of iron.

**Estimation of Iron.**—10 c.c. of the syrup are mixed with 30 c.c. of water and boiled with 2 grams potassium chlorate and 60 c.c. standard thiosulphate solution; the solution is filtered, the precipitate washed and dissolved in dilute hydrochloric acid, and the iron precipitated as hydrate, and estimated as  $\text{Fe}_2\text{O}_3$ .

**Estimation of Iodine.**—5 c.c. of the syrup are distilled with 15 c.c. water and 2 grams potassium chlorate, and the distillate collected in a solution of potassium iodide (2 grams). When nearly all the iodine has passed over, the receiver is changed, and the distillation continued until a colourless distillate is obtained. The distillates are then mixed and titrated with standard thiosulphate solution.

The direct estimation of the iodine by boiling the syrup with potassium chlorate and a known excess of standard thiosulphate solution, and estimating the amount of the latter used, did not yield trustworthy results, owing to the decomposition which a solution of sodium tetrathionate undergoes when boiled.

By allowing iodine to stand in contact with excess of metallic iron, bubbles of gas are evolved, and the solution appears to be deficient in iron. Experiments were made with iron wire and reduced iron, when it was found that the solution made with iron wire lost, after 9 hours' standing, 4.7 per cent., and after 7 days 5.5 per cent. The other solution lost in the first case 9.4 per cent., and the second 39.7. This reaction requires further investigation. L. T. O'S.

**Presence of Nitrogen in Iron and Steel.** By A. H. ALLEN (*Chem. News*, 41, 231—234).—As tests for or modes of determining nitrogen in iron and steel the following principles have been utilised:—

1. Ignition with soda-lime or potash-baryta, in order to produce ammonia (Schafhäütl, Marchand).

2. Heating to redness in a current of hydrogen to produce ammonia (Frémy, Stuart and Baker).

3. Dissolving in an acid, and distilling off the resultant ammonia after addition of an alkali (Boussingault, Bouis).

4. Ignition in a vacuum with cupric oxide, and measuring the liberated nitrogen as gas (Schafhäütl, Marchand).

5. Ignition with native mercuric sulphide and measuring as gas (Boussingault).

6. Ignition with potassium or sodium, forming a cyanide (Marchand).

In 1865, Stahlschmidt prepared a definite nitride of the formula  $\text{N}_2\text{Fe}_4$ , and concluded that nitride of iron existed in an irregular state of distribution in commercial steel.



With a view to produce ammonia from the nitrogen in steel, and at the same time avoid the difficulties attending the process of heating in a current of hydrogen, the steel or iron under examination is heated in a current of steam, the hydrogen being in a nascent state, and the ammonia being produced in a neutral atmosphere, and at once removed from the sphere of action before the high temperature has decomposed it.

The apparatus employed consists of a piece of combustion tubing (about 7 feet), bent about the centre at an obtuse angle, one limb being encased in a Liebig's condenser, the other fitted to a retort containing water, to which a few drops of hydrochloric acid and some steel borings had been added; in the tubulure of the retort is a cork with a tube passing through, and with a clip at the outer side.

The limb of the combustion tube, in connection with the retort, contains the metal to be operated on, retained in its proper position by two platinum gauze plugs.

To perform an experiment, 50 to 200 grams of the steel borings are placed in the limb adjoining the retort, the water in the retort is boiled until steam blows out uncondensed at the other end; water is now passed through the Liebig's condenser, and the distillate is collected and tested by Nessler until free from ammonia; as soon as free the limb containing the metal is raised to a red heat, a fresh quantity of ammonia is now evolved which is estimated by Nessler. In all cases the iron or steel, before being placed in the apparatus, was heated to redness in a muffle. In addition to Nessler's test, the condensed steam was proved to contain ammonia by the ordinary tests for that body.

By arranging the apparatus as usual, and filling the space between the platinum plugs with hæmatite ore, passing steam, raising to a red heat, reducing the hæmatite by means of hydrogen, and then passing steam again, it was shown that no ammonia was produced, *i.e.*, that iron reduced by hydrogen was free from nitrogen. Some nitride of iron, prepared by heating iron in ammonia, was placed in the apparatus, and on passing steam, ammonia was given off even at 100°, the amount being much greater on heating to redness. Dissolving the steel in hydrochloric acid affords the most convenient and satisfactory means of converting the contained nitrogen into ammonia. The method of experimenting is to take 1 gram of the iron or steel, heat it to redness in a muffle, and tip it into a flask containing ammonia-free water; the flask is then connected with a globe-shaped separating funnel with a tap in the stem, the funnel contains a number of recently ignited glass beads; the water in the flask is now boiled until a current of steam issues from the mouth of the funnel, when the tap is closed and the lamp removed. 20 c.c. of hydrochloric acid (sp. gr. 1.11) are now poured into the funnel, the mouth of which is closed by a cork fitted with a glass tube that terminates under the surface of mercury; the acid is boiled until all air is expelled and is then run into the flask, the contents of which, together with the rinsings of the funnel when the steel is dissolved, are washed into a retort, distilled with quicklime, and the resulting ammonia determined by Nessler in the usual manner. The greatest care was exercised to obtain all the

reagents employed free from ammonia, and blank experiments were performed from time to time for verification, correction being made for the minute proportion of ammonia found in this way.

It is found that the presence of air exerts no influence on the amount of nitrogen found.

A table, with the results of some 20 specimens of iron and steel and other metals, is given, in which the proportion of nitrogen varies from 0.0041 per cent. in spiegeleisen, to 0.0172 per cent. in steel from Dannemora iron.

No nitrogen was present in the specimens of commercial aluminium, zinc, and nickel examined by the solution method, and but very small proportions were found in magnesium and sodium. Hence iron is exceptional in the proportion of nitrogen contained in it.

F. L. T.

**Estimation of Total Carbon in Iron and Steel.** By S. C. JUTSUM (*Chem. News*, 41, 17).—Weyl's method for solution of the metal is recommended (*Pogg.*, 114, 507). The decomposition cell is made of a 5-oz. beaker containing hydrochloric acid (1 concentrated acid to 3 water): into this dips a beaker without a bottom, between the beakers is placed the positive platinum electrode. The steel bar to be dissolved is ground bright, weighed, covered with rubber sheeting to within an inch of the lower end, with the exception of a part where a binding screw is attached, and immersed in the acid. A single Grove's cell is recommended to be used; solution may be allowed to proceed over night. The separated carbon is filtered through a glass tube containing fine sand and glass wool covered at its lower end by filter-paper, muslin, and wire-gauze; the tube is inserted through a cork into a bottle which communicates with an exhausting pump. No carbon passes through this filter; the filtration and washing, first with water, then with caustic soda, and finally with water, is complete in 10 minutes.

The covering at the bottom of the filter is removed, a little glass wool placed at the top of the carbon, and the whole contents of the tube pushed out into an Ullgren's apparatus, wherein the carbon is oxidised and weighed as carbonic anhydride.

M. M. P. M.

**Estimation of Carbon in Steel.** By J. W. WESTMORELAND (*Chem. News*, 41, 152).—In reply to Sergius Kern (*Chem. News*, 40, 225) the author states that the colour test for carbon gives results agreeing with the combustion process, and gives data in support of his assertion. It does not give good results with high or very low percentages of carbon, but it is invaluable for estimations ranging from 0.1 to 1.0 per cent.

F. L. T.

**Electrolytic Estimation of Nickel and Cobalt.** By H. FRESSENTUS and F. BERGMANN (*Zeits. Anal. Chem.*, 1880, 314—324).—Very accurate results are obtained by the electrolytic precipitation of nickel and cobalt, either together or separately, from solutions which contain in 200 c.c., 0.1—0.15 gram of metal as sulphate, 2.5—4 grams of ammonia ( $\text{NH}_3$ ), and 6—9 grams of ammonium sulphate. The electrodes of which the negative is a platinum cone, the positive a wire

3 g 2

spiral, are placed  $\frac{1}{3}$ — $\frac{1}{2}$  cm. apart, and the current—best generated by a Clamond's thermopile—should be of such strength as to yield by decomposition of water 200 c.c. of mixed gases in an hour. The precipitation takes 5—6 hours. The completion of precipitation can be ascertained by adding a few drops of solution of ammonium sulphocarbonate, which should only give an extremely faint tinge, rose colour with nickel, wine yellow for cobalt. Deficiency of ammonia injures the results, excess has no effect beyond increasing the time necessary for complete precipitation. Ammonium carbonate can be substituted for the sulphate, but retards the operation; ammonium chloride or nitrate almost entirely prevents the precipitation. A. J. G.

**Volumetric Estimation of Lead.** By W. DIEHL (*Zeits. Anal. Chem.*, 1880, 306—309).—The lead having been separated from the other metals in the ore by precipitation as sulphate, is dissolved in ammonium acetate, excess of  $\frac{1}{2}$ th normal solution of potassium dichromate is then added, together with a few drops of acetic acid, and the plumbic chromate filtered off, after standing for about half an hour. The excess of dichromate in solution is then determined by adding sulphuric acid, heating to boiling and titrating with standard sodium thiosulphate;  $\frac{1}{4}$  mols. of dichromate are reduced by 3 mols. of thiosulphate. The results are accurate. A. J. G.

**Detection and Estimation of Arsenic.** By T. D. BOEKE (*Chem. News*, 41, 177—178).—For the detection of arsenic the author prefers Marsh's method, provided the organic matter be removed; this may be done by ignition with potassium nitrate and sodium carbonate, or by heating with sulphuric and a little nitric acid until the mass is wholly converted into a porous coal. The author prefers the latter method.

For estimation in organic mixtures, the author digests with potassium chlorate and hydrochloric acid, filtering off any insoluble residue; the solution after neutralisation with sodium carbonate and concentration is again acted on by potassium chlorate and hydrochloric acid, saturated with ammonia, precipitated by "magnesia" mixture and allowed to stand 24 hours; the magnesia precipitate is dissolved in dilute sulphuric acid, sulphuretted hydrogen passed, and the arsenic weighed as arsenious sulphide. F. L. T.

**Detection of Bismuth.** By J. C. THRESH (*Pharm. J. Trans.* [3], 10, 641).—Minute traces of bismuth may easily be detected by adding potassium iodide to the solution rendered slightly acid by hydrochloric acid, when an orange to a yellow coloration is produced according to the quantity of bismuth present; 1 part of bismuth in a million gives a decided yellow coloration. The presence of mercury, lead, and antimony slightly interferes with the test. Mercuric iodide is, however, soluble in excess of potassium iodide and lead iodide on warming the solution; in each case, bismuth being present, the coloration is produced. In presence of antimony the potassium iodide must not be added in excess, as large quantities of the reagent give a reddish-yellow coloration with antimony itself. Bismuth does not give a

coloration with potassium iodide in neutral or alkaline solutions; if sulphuric acid is present in excess it is necessary first to neutralise the acid with ammonia, and then acidify with hydrochloric acid, otherwise a dark-brown precipitate is formed.

To detect bismuth by this method in a mixture of salts, dissolve in hydrochloric acid the precipitate produced by adding ammonia to the nitric acid solution of the sulphides insoluble in ammonium sulphide, in one portion test for lead, and in the other for bismuth, with potassium iodide.

L. T. O'S.

**Method for Estimating Bismuth Volumetrically.** By M. KUHARA (*Chem. News*, 41, 153—154).—The method consists in precipitating the bismuth from its nitric acid solution by adding disodium arsenate of known strength in slight excess, allowing to stand until the reaction is completed; making alkaline with ammonia, then acid with acetic acid, and estimating the excess of arsenate by standard uranium nitrate, using potassium ferrocyanide as indicator.

The disodium arsenate (about 21 grams per litre) was standardised on known quantities of bismuth; the strength of uranium nitrate that gave the best results was 43.2 grams of the crystallised salt per litre; it was standardised on the disodium arsenate.

The average error of six results obtained by working on known weights of bismuth is .3 per cent. on total quantity.

F. L. T.

**Modification of Dumas' Method for Estimating Nitrogen.** By K. ZULKOWSKY (*Ber.*, 13, 1096—1103).—Several improvements in the author's (*Annalen*, 182, 296) modification of Dumas' method of estimating nitrogen in carbon compounds is described, the more important of which are as follows:—

In the old form of apparatus, the potash-solution for absorbing the carbonic acid was very apt to run back when the current of gas was not evolved with sufficient regularity; this is now avoided by inserting a Bunsen's valve between the combustion tube and the azotometer. The frequent emptying and refilling of the measuring tube is also rendered unnecessary by a different manipulation of the apparatus. According to the old method of operating, the combustion tube, sealed at one end, was first partially filled with sodium bicarbonate, for the evolution of carbonic anhydride, to drive out the air, and then with the mixture of the substance with copper oxide. The result of this was that fresh copper oxide had to be employed for each determination, thus requiring much time and material. In order to avoid this, the operation is conducted like an ordinary combustion, the combustion tube being open at both ends, and connected at the end removed from the azotometer, with a separate tube containing the sodium bicarbonate for the evolution of carbonic anhydride. This arrangement allows of the substance being placed in a boat as in an ordinary combustion with an open tube, and hence the same tube and the same lot of oxide of copper may be used many times in succession without any re-arrangement, except the reoxidation of the copper in a current of air, and the reduction of the copper coil in a current of hydrogen. The apparatus thus consists of three parts: (1) the carbonic anhydride

generator; (2) the combustion tube; (3) the azotometer. For the *modus operandi* reference must be made to the original paper. By this apparatus nitrogen determinations can be made with very great exactness and in a very short time, viz., 1 to 1½ hours. T. C.

*Abstractor's Note.*—The introduction of a separate tube for the generation of the carbonic anhydride, as well as several other important improvements, has also been proposed by Groves (this Journal, 1880, Trans., 500).—T. C.

**Proximate Analysis of Plants.** By H. B. PARSONS (*Pharm. J. Trans.* [3], 10, 793—797).—*Estimation of Moisture.*—2 grams of the finely powdered specimen are dried at 100—120°; the loss gives moisture, and sometimes a little volatile oil. In some cases it is necessary to dry at lower temperature, or in a current of hydrogen or carbonic anhydride.

*Estimation of Ash.*—2 grams are gently ignited at a faint red heat until quite free from carbonaceous matter.

The residue is extracted with water, dilute hydrochloric acid, and concentrated alkali in succession, and the residue in each case weighed.

*Total nitrogen* is estimated by ignition with soda-lime. If the nitrogenous matter present is albuminoid, its amount is obtained by multiplying the amount of nitrogen by 6.25.

*Benzene Extract.*—5 grams are digested with benzene (b. p. 80—85°) for six hours, whereby certain volatile oils, resins, camphors, organic acids, wax, fats, oils, chlorophyll and other colouring matters, alkaloids, and glucosides are extracted.

The solution is evaporated to dryness, and the weighed residue treated with water and again evaporated; the residue dried at 110° and weighed: loss in weight gives volatile oils. If the presence of volatile alkaloids is suspected, a few drops of hydrochloric acid are added previous to evaporation. Treat the residue with warm water, leave it to cool, and filter. In one half of the filtrate determine total organic matter and ash; in the other half test for alkaloids, glucosides, and organic acids. Dissolve the residue in benzene, evaporate the solution to dryness, and extract the residue with hydrochloric acid; filter and test for alkaloids and glucosides in the filtrate. Treat the residue several times with a large excess of alcohol. Evaporate the solutions and estimate the extracted matter, which usually consists of chlorophyll and one or more resins; these may sometimes be separated by light petroleum, naphtha, or chloroform. Animal charcoal removes chlorophyll and some resins. Camphor, if present in the plant, will be found for the most part in the alcoholic extract.

It is sometimes advisable to exhaust the plant with light petroleum before proceeding with benzene. Where pure benzene cannot be obtained, chloroform serves as the best substitute.

*Alcoholic Extract.*—The residue from the extraction with benzene is dried at 100°, and digested for 1½ hours with alcohol (80 per cent.). The solution is concentrated and left at rest, and any crystals or precipitate which may form are separated. The solution is made up to a

definite volume, and in a measured portion the total organic matter and ash determined. In another the total organic matter and ash soluble in water are determined, and by difference, the same insoluble in water.

The remaining solution is evaporated to dryness, and the residue treated with several portions of absolute alcohol.

*A. Soluble in Absolute Alcohol.*

(a.) Soluble in water.

*Precipitated by Subacetate of Lead.*

Tannin and most organic acids, some extractives, and inorganic acids. Weigh precipitate, ignite and weigh: loss equal to organic matter.

*Not Precipitated by Subacetate of Lead.*

Alkaloids, glucosides, extractives and colours.

(b.) Insoluble in water.

*Soluble in Dilute Hydrochloric Acid.*

Alkaloids, glucosides, some extractives: determine insoluble portion.

*Soluble in Dilute Ammonia.*

Most acid resins, some colours.

*Insoluble in Dilute Ammonia.*

Neutral resins, colours, and albuminoids. Dissolve residue in alcohol. Evaporate and weigh.

*B. Insoluble in Alcohol.*

(c.) Soluble in Water.

*Precipitated by Subacetate of Lead.*

Some colours, extractives, albuminoids, organic and inorganic acids. Weigh, ignite, and weigh again. Loss gives organic matter.

*Not Precipitated by Subacetate of Lead.*

Alkaloids, glucose, saccharose extractives. Determine by difference. Separate lead from solution, and determine saccharose and glucose with Fehling's solution.

(d.) Insoluble in Water.

*Soluble in Dilute Hydrochloric Acid.*

Some alkaloids and glucosides. Determine by difference.

*Insoluble in Dilute Hydrochloric Acid.*

A few resins, extractives, and colours. Dissolve in alcohol. Evaporate solution and weigh.

When the plant contains much tannin or sugar, the following method for analysing the alcoholic extract should be adopted.

Dilute the extract to 200 c.c. with alcohol (80 per cent.). In 20 c.c. determine total organic matter and ash; in 20 c.c. determine organic

matter and ash, soluble and insoluble in water. Evaporate the remaining 160 c.c. to dryness, heat the residue with water, filter and make the filtrate up to 160 c.c.

The residue may contain resins, colours, and glucosides, which may be removed by dilute ammonia; alkaloids and some glucosides soluble in dilute hydrochloric acid; also insoluble albuminoids and resins.

In 20 c.c. of the filtrate the tannin is determined by A. Carpeni's method (*Chem. News*, July 9, 1875, p. 19). 20 c.c. are precipitated with normal lead acetate. The precipitate, which may contain tannin, gallic and other organic acids, inorganic acids, albuminoids, extractives, and some colours, is dried at 100–120° and weighed.

20 c.c. are precipitated with subacetate of lead, and the precipitate is weighed. A greater number of acids, extractives, and colours are precipitated by this reagent than by the former. To the filtrate add excess of hydrochloric acid, boil, and determine the glucose in the solution.

Precipitate another 20 c.c. with subacetate from the filtrate, remove the lead with sodium carbonate, and determine the glucose in the solution. Any appreciable difference between this result and the former is due to the presence of glucosides or saccharose.

A further 20 c.c. is precipitated with subacetate of lead, and the organic acids in the precipitate determined after the removal of the lead by sulphuretted hydrogen. Add sulphuric acid to the filtrate and an equal volume of alcohol, allow the solution to stand two hours, filter, evaporate the filtrate to expel alcohol, and test the solution for alkaloids, glucosides, sugars, and extractives.

*Aqueous Extract.*—The residue from the alcoholic extract is exhausted with cold water. When the plant contains much gummy substance, this is best done by adding a measured volume of cold water to the residue, and leaving it from six to twelve hours. Filter through linen, and in a measured portion of the solution estimate the total organic matter and ash. In the case of fruits and fleshy roots, pectin bodies, organic acids, albuminous substances, colouring matters and sometimes a body resembling dextrin are found in this residue, but otherwise it generally consists of gum.

*Acid Extract.*—The residue insoluble in water is boiled for six hours with 500 c.c. water and 5 c.c. sulphuric acid (sp. gr. 1.34). By this means all the starch is converted into glucose, which is estimated with Fehling's solution, the result multiplied by .9 equals starch and its isomerides; the insoluble residue is weighed.

*Alkali Extract.*—The residue is boiled with 500 c.c. of a 2 per cent. solution of caustic soda. The extract usually contains albuminous matter, modifications of pectic acid, Frémy's "cutose," humus, and decomposition products.

The residue, which consists of cellulose, is bleached with chlorine and caustic soda and weighed.

Benzene, alcohol, and water remove from most plants the substances of the greatest chemical and medical interest, but in the case of grain fodder and foods, the substances extracted by acids and alkalis have great value.

L. T. O'S.

**Use of the Spectroscope in Discriminating Anthracenes.** By B. NICKELS (*Chem. News*, 41, 52 and 95).—Those substances associated with commercial anthracene, which yield “amorphous particles” on oxidation, are characterised by showing absorption-bands between F and G, and immediately to the left of G (D at the right hand). Commercial anthracene may be tested by dissolving a few decigrams in 6 c.c. benzene, and placing the solution between a lamp and the slit of a direct vision spectroscope. Absence, or faintness of absorption-bands, points to absence of impurities; the comparative purity of samples may be judged of from the depth and intensity of the absorption bands. M. M. P. M.

**Estimation of Glycerol.** By W. LENZ (*Zeits. Anal. Chem.*, 1880, 297—305).—The author has determined the specific gravity of mixtures of glycerol and water, and their refractive indexes at 12·5—12·8°. In the following table the specific gravity is given:—

| Anhydrous glycerol, per cent. | Specific weight at 12—14°. | Anhydrous glycerol, per cent. | Specific weight at 12—14°. | Anhydrous glycerol, per cent. | Specific weight at 12—14°. |
|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|
| 100                           | 1·2691                     | 67                            | 1·1795                     | 34                            | 1·0880                     |
| 99                            | 1·2664                     | 66                            | 1·1764                     | 33                            | 1·0852                     |
| 98                            | 1·2637                     | 65                            | 1·1733                     | 32                            | 1·0825                     |
| 97                            | 1·2610                     | 64                            | 1·1702                     | 31                            | 1·0798                     |
| 96                            | 1·2584                     | 63                            | 1·1671                     | 30                            | 1·0771                     |
| 95                            | 1·2557                     | 62                            | 1·1640                     | 29                            | 1·0744                     |
| 94                            | 1·2531                     | 61                            | 1·1610                     | 28                            | 1·0716                     |
| 93                            | 1·2504                     | 60                            | 1·1582                     | 27                            | 1·0689                     |
| 92                            | 1·2478                     | 59                            | 1·1556                     | 26                            | 1·0663                     |
| 91                            | 1·2451                     | 58                            | 1·1530                     | 25                            | 1·0635                     |
| 90                            | 1·2425                     | 57                            | 1·1505                     | 24                            | 1·0608                     |
| 89                            | 1·2398                     | 56                            | 1·1480                     | 23                            | 1·0580                     |
| 88                            | 1·2372                     | 55                            | 1·1455                     | 22                            | 1·0553                     |
| 87                            | 1·2345                     | 54                            | 1·1430                     | 21                            | 1·0525                     |
| 86                            | 1·2318                     | 53                            | 1·1403                     | 20                            | 1·0498                     |
| 85                            | 1·2292                     | 52                            | 1·1375                     | 19                            | 1·0471                     |
| 84                            | 1·2265                     | 51                            | 1·1348                     | 18                            | 1·0446                     |
| 83                            | 1·2238                     | 50                            | 1·1320                     | 17                            | 1·0422                     |
| 82                            | 1·2212                     | 49                            | 1·1293                     | 16                            | 1·0398                     |
| 81                            | 1·2185                     | 48                            | 1·1265                     | 15                            | 1·0374                     |
| 80                            | 1·2159                     | 47                            | 1·1238                     | 14                            | 1·0349                     |
| 79                            | 1·2132                     | 46                            | 1·1210                     | 13                            | 1·0322                     |
| 78                            | 1·2106                     | 45                            | 1·1183                     | 12                            | 1·0297                     |
| 77                            | 1·2079                     | 44                            | 1·1155                     | 11                            | 1·0271                     |
| 76                            | 1·2042                     | 43                            | 1·1127                     | 10                            | 1·0245                     |
| 75                            | 1·2016                     | 42                            | 1·1100                     | 9                             | 1·0221                     |
| 74                            | 1·1999                     | 41                            | 1·1072                     | 8                             | 1·0196                     |
| 73                            | 1·1973                     | 40                            | 1·1045                     | 7                             | 1·0172                     |
| 72                            | 1·1945                     | 39                            | 1·1017                     | 6                             | 1·0147                     |
| 71                            | 1·1918                     | 38                            | 1·0989                     | 5                             | 1·0123                     |
| 70                            | 1·1889                     | 37                            | 1·0962                     | 4                             | 1·0098                     |
| 69                            | 1·1858                     | 36                            | 1·0934                     | 3                             | 1·0074                     |
| 68                            | 1·1826                     | 35                            | 1·0907                     | 2                             | 1·0049                     |
| 67                            | 1·1795                     | 34                            | 1·0880                     | 1                             | 1·0025                     |



**Detection of Starch-sugar Mechanically Mixed with Refined Cane-sugar.** By P. CASAMAJOR (*Chem. News*, 41, 221—222).—The processes given are the saccharimetric, before and after inversion; the reduction with Fehling's solution; the solubility in cold water, the starch-sugar dissolving but slowly, and appearing as white specks like crushed wheat, and the taste; in the last case comparison must always be made with a sample of refined sugar. F. L. T.

**Action of Bone-black on Sugar Solutions.** By P. CASAMAJOR (*Chem. News*, 41, 66).—Dried, newly made bone-black, when kept in contact with a solution of pure sugar, absorbs 0.006 per cent. (of its own weight.) Filtration of sugar solutions through bone-black does not therefore interfere with subsequent testing by the optical method. M. M. P. M.

**Behaviour of Various Sugars with Alkaline, Copper, and Mercury Solutions.** By F. SOXHLET (*J. pr. Chem.* [2], 21, 227—317).—The preparation of the various sugars in a state of purity is described at some length.

An abstract of a previous paper by Soxhlet has already been given in this volume (p. 66). Soxhlet shows that the quantities of copper reduced under like conditions by the various sugars from Fehling's or Löwe's solutions, differ among themselves, and that the quantity for any individual sugar depends on the strength of the solution, and the amount of copper present in excess. In no case does one equivalent of a sugar reduce 10 equivalents of cupric oxide. He prefers as before (*loc. cit.*) to keep his Fehling's test in two separate solutions, only mixing immediately before use.

The reducing power of a sugar is volumetrically determined in the following manner:—Varying quantities of the copper solution were heated to boiling in a dish, equal volumes of the solution of Rochelle salt and sodium hydrate being previously added. Then 50 c.c. or 100 c.c. of the 1 per cent. or  $\frac{1}{2}$  per cent. sugar solutions respectively were added, and the whole was boiled for two, four, or six minutes, according to the variety of the sugar. The contents of the dish are then thrown on a filter, the filtrate is acidified with acetic acid, and potassium ferrocyanide at once added to ascertain the presence of copper. This process is repeated until two quantities of the copper solution, differing from each other by  $\frac{1}{10}$  c.c., give, the one a filtrate containing copper, the other a filtrate free from copper. The mean of these two readings is taken as the result.

The gravimetric method of determining the copper reduced by the sugars acting on Fehling's or Löwe's solution is to boil a measured quantity of the sugar-solution with an excess of the Fehling's or Löwe's solution, and then to filter by means of gentle suction, through a weighed tube filled with asbestos; wash with hot water, then with absolute alcohol, and finally ether. On passing hydrogen through the heated tube, the cuprous oxide is reduced to the metallic state in two or three minutes, and then weighed. The following are the chief results:—

*Dextrose*.—0.5 gram in 1 per cent. solution reduces 105.2 c.c. Fehling (undiluted), or 101.1 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 10.52—1 : 10.11.

*Invert sugar* (i.e., equal molecules of dextrose and levulose obtained by the action of acids on cane-sugar).—0.5 gram in 1 per cent. solution reduces 101.2 c.c. Fehling (undiluted), or 97.0 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 10.12—1 : 9.7.

In the case of dextrose and invert sugar, dilution of the solution lowers, excess of copper raises, the reducing power.

*Milk-sugar*.—0.5 gram in 1 per cent. solution reduces 74 c.c. Fehling.

Ratio of reduction, 1 : 7.4.

Dilution has no noteworthy influence on the reducing power. Excess of copper raises it, but to a much slighter extent than with dextrose or invert sugar.

*Galactose*.—0.5 gram in 1 per cent. solution reduces 98 c.c. Fehling (undiluted), or 94 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 9.8—1 : 9.4.

Dilution lessens the reducing power to the same extent as with dextrose and invert sugar. Excess of copper raises the reducing power, but to a somewhat slighter extent than with dextrose and invert sugar.

*Levulose* (calculated from the results with dextrose and invert sugar).—0.5 gram in 1 per cent. solution, reduces 97.2 c.c. Fehling (undiluted), or 93 c.c. Fehling (diluted with 4 volumes of water).

Ratio of dilution, 1 : 9.72—1 : 9.3.

Dilution and excess of copper act respectively as with dextrose and invert sugar. The reducing power of levulose is probably equal to that of galactose.

*Inverted Milk-sugar*.—Reducing power equal to that of invert sugar (Rodewald).

*Maltose*.—0.5 gram in 1 per cent. solution reduces 64.2 c.c. Fehling (undiluted), or 67.5 c.c. Fehling (diluted with 4 volumes of water).

Ratio of reduction, 1 : 6.09—1 : 6.41.

Dilution raises the reducing power. Excess of copper has no effect with undiluted Fehling, but in highly dilute solutions raises the reducing power to a slight extent.

With the exception of the determination of sugar in diabetic urine (where, owing to the constant formation of ammonia, some of the cuprous oxide is dissolved and passes through the filter, and consequently the end of the reaction must be decided, as usual, by the disappearance of the blue colour), the following plan is adopted for the estimation of the various sugars. The approximate strength of the sugar solution is first determined in the usual manner, by the disappearance of the blue, operating on 25 c.c. Fehling. The sugar solution is now diluted so as to contain 1 per cent. of the sugar, and the determination is proceeded with as described above, operating on 50 c.c. Fehling, undiluted with water.

In the case of highly coloured fluids, the indication with potassium ferrocyanide is difficult to recognise, the reaction with sulphuretted

hydrogen giving still worse results. In such cases the following device is adopted:—The filtrate is boiled with a few drops of the sugar solution in a beaker, allowed to settle, and then poured off; on wiping the bottom and sides of the beaker with a piece of white filter-paper, it will be coloured red if any copper still remain in the solution.

The behaviour of the sugars with alkaline mercury solutions was tested both with Knapp's solution (alkaline mercuric cyanide), and Sachsse's solution (alkaline mercuric iodide in potassium iodide).

It is found as observed by Brumme (*J. pr. Chem.* [2], 21), that different results are obtained from Knapp's solutions, according as the sugar solution is added gradually, or all at once; when gradually added more sugar being required; with Sachsse's, however, the reverse is the case.

To get comparable results the sugar must be added all at once, the solution boiled for two or three minutes, and the liquid tested for mercury, always using the same indicator; in using the alkaline tin solution as indicator, 0.200—0.202 gram of grape-sugar were always required for 100 c.c. Knapp, in a large number of experiments. It is remarkable that these two solutions, although containing almost exactly the same amount of mercury, require very different quantities of sugar to reduce equal volumes of them. This is shown to be due, to a great extent, to the different amounts of alkali present in them.

The amounts of mercury solutions which 1 gram of sugar in 1 per cent. solution reduces are:—

|                       |                     |                       |
|-----------------------|---------------------|-----------------------|
| Grape-sugar .....     | 497.5 c.c. (Knapp), | 302.5 c.c. (Sachsse). |
| Invert sugar .....    | 502.5        "      | 376.0        "        |
| Levulose .....        | 508.5        "      | 449.5        "        |
| Milk-sugar .....      | 322.5        "      | 214.5        "        |
| Galactose .....       | 413.0        "      | 226.0        "        |
| Inverted milk-sugar.. | 448.0        "      | 258.0        "        |
| Maltose .....         | 317.5        "      | 197.6        "        |

The various sugars have different reducing powers for the alkaline mercury solutions, and there is no definite relation between the amounts of Knapp's and Sachsse's solutions required by them; the amount of Sachsse's solution, to which 100 c.c. Knapp's correspond, varying from 54.7 c.c. in the case of galactose, to 74.8 c.c. in the case of invert sugar.

Taking the reducing power of grape-sugar = 100, the reducing powers of the other sugars are:—

|                        | Fehling (undiluted). | Knapp.        | Sachsse. |
|------------------------|----------------------|---------------|----------|
| Grape-sugar .....      | 100                  | 100           | 100      |
| Invert sugar .....     | 96.2                 | 99.0 (100 ?)  | 124.5    |
| Levulose (?) .....     | 92.4                 | 102.2 (100 ?) | 148.6    |
| Milk-sugar .....       | 70.3                 | 64.9          | 70.9     |
| Galactose.....         | 93.2                 | 83.0          | 74.8     |
| Inverted milk-sugar .. | 96.2                 | 90.0          | 85.5     |
| Maltose .....          | 61.0                 | 63.8          | 65.0     |

The two mercury methods have no advantage in point of accuracy

or convenience over Fehling's method, the latter having the preference on account of the great certainty of the point at which the reduction is finished.

The mercury methods are, however, of great importance, both for the identification of a sugar and for the estimation of two sugars in presence of each other, as already proposed by Sachsse. For instance, for the estimation of grape and invert sugars in presence of each other, we have the two equations:  $ax + by = F$ ,  $cx + dy = S$ . Where—

|     |   |  |                          |                 |               |
|-----|---|--|--------------------------|-----------------|---------------|
| $a$ | = | number of l c.c. Fehling, reduced by 1   | gram                     | grape-sugar.    |               |
| $b$ | = | "  | "                        | invert sugar.   |               |
| $c$ | = | "  | Sachsse                  | "               | grape-sugar.  |
| $d$ | = | "  | "                        | "               | invert sugar. |
| $F$ | = | "  | Fehling, used for 1 vol. | sugar solution. |               |
| $S$ | = | "  | Sachsse                  | "               | "             |
| $x$ | = | amount of grape-sugar in grams in 1 vol. | of the solution.         |                 |               |
| $y$ | = | "  | invert sugar             | "               | "             |

It need scarcely be mentioned that the above, together with all other indirect methods, leaves room for increased accuracy; but nevertheless the combination of a mercury method with a copper method in the determination of a sugar whose nature is not exactly known, gives a more serviceable result than the hitherto adopted plan, by which a solution that reduced 10 c.c. Fehling was said to contain .05 gram of "sugar." F. L. T.

**Cupric Test Pellets for Sugars.** (*Chem. News*, 41, 63).—The solid ingredients of the ordinary copper test for sugar have been compressed into pellets by Dr. Pavy. When required for use a pellet is dissolved in about 3 c.c. of rain water. M. M. P. M.

**Report on the Methods of Estimating Cellulose and on their Defects.** By C. KRAUCH (*Landw. Versuchs.-Stat.*, 24, 295—299).—The so-called "non-nitrogenous extract," separated in the ordinary course of analysis from cellulose by successive treatment with potash and sulphuric acid, in reality contains a large amount of cellulose, varying in quantity with the strength of the solution employed. Although the practical value of the analysis is not influenced by this result, since experiment shows that the sum of the digestible parts of the so-called extract and of the cellulose is about equal to the quantity set down as non-nitrogenous extract, an incorrect idea is nevertheless given of the quality and constitution of the substance under investigation. Rye, hay, and clover hay, which had been freed from starch, fat, and protein, were boiled with potash and sulphuric acid solutions, and it was found that 80 per cent. of the total cellulose and fibre in the case of rye, and 50 per cent. in the case of hay and dried clover, had gone into solution; the composition of the dissolved cellulose was not constant, varying considerably in the case of hay and clover.

J. K. C.

**Estimation of Fat in Milk.** By P. VIETH (*Bied. Centr.*, 1880, 302—303).—The "lactobutyrometer," it is suggested, will be found to supply the want of a ready and accurate dairy method of estimating the fat in milk (see also *Bied. Centr.*, 1876, 231; 1877, 226; 1879,

770). The results obtained with the creamometer are shown to be too much influenced by temperature to be of any value.

A. J. C.

**Saponification of Fats.** By VON DER BECKE (*Zeits. Anal. Chem.*, 1880, 291—297).—The saponifying action of lead oxide, of potassium hydrate, and of lime, is very different, the amounts of glycerol liberated especially differing, as shown in the accompanying extract from the author's table.

*Percentage of Glycerol.*

|                   | Butter. | Cacao fat. | Tallow. | Grease | Olive oil. | Rapeseed oil. | Linseed oil. |
|-------------------|---------|------------|---------|--------|------------|---------------|--------------|
| Lead oxide . . .  | 7 98    | 0 23       | 0 13    | 6 6    | 3 76       | 4 2           | 4 4          |
| Potassium hydrate | 10 59   | 5 99       | 7 64    | 8 27   | 6 41       | 4 58          | 6 2          |
| Lime . . . . .    | 7 99    | 2 19       | 2 43    | 9 27   | —          | —             | —            |

A. J. G.

**Estimation of Fat in Fodder.** By P. WAGNER (*Landw. Versuchs.-Stat.*, 24, 289—294).—Three or four hours' treatment with ether is generally considered sufficient for the extraction of fat from organic bodies. The time is, however, too short, as the following experiment shows. Palm cake was extracted with ether by Storch's method:—

|                              |       |                  |
|------------------------------|-------|------------------|
| After 3 hours, was extracted | 11·88 | per cent of fat. |
| „ 3 hours further . . . .    | 0·54  | „                |
| „ 6 „ . . . .                | 0·33  | „                |
| „ 15 „ . . . .               | 0·47  | „                |
| „ 10 „ . . . .               | 0·01  | „                |

Altogether, after 37 hours, 13·23 per cent. of fat was extracted.

The same sample yielded 12 per cent. of fat when allowed to stand two days with ether in the cold.

It was found that treatment with small quantities of ether at a time was not sufficient, even after 21 days' standing, to extract the whole of the fat; relatively large volumes of ether seem to be necessary to break up the fat-cells.

The above experiments were carried on with a material containing 9 per cent. of water, the action of absolute ether on the dried substance was then tried. The fodder was dried over a water-bath, and after 27 hours' treatment with absolute ether, yielded 10 54 per cent. of fat. The same dried over sulphuric acid, and treated similarly, gave 10·73 per cent., and when allowed to stand with absolute ether in the cold, 10·4 per cent. was obtained; common ether, on the other hand, extracting 11·35 per cent. Undried material treated 27 hours with absolute ether, yielded 10·74 per cent., and with common ether, 13·01 per cent. of fat. It seems, therefore, that water must be present both in the material and in the ether, in order that the whole of the fat may be extracted.

J. K. C.

**Detection of Wax.** By E. HIRSCHSOHN (*Pharm. J. Trans.* [3], 10, 749—751).—As the result of a series of experiments on different kinds of wax, the author submits the following method for their detection.

The wax is boiled with ten times its volume of chloroform, until it is completely dissolved, and the solution is then cooled.

I. The solution remains clear after cooling.

(A.) Ether dissolves the wax completely.

(a.) Alcoholic ferric chloride gives a precipitate with alcoholic solution of wax, insoluble on boiling. *Wax from Myrica quercifolia.*

(b.) Ferric chloride gives black coloration. *Wax from undetermined species of Myrica.*

(c.) Ferric chloride gives brown coloration. *Wax from Myrica cerifera. Wax from Orizaba.*

(B.) Wax only partly soluble in ether. Boil with ten times its volume of alcoholic potash, and heat the soap with 100 volumes of water.

(a.) Soap is soluble. Japanese wax.

(b.) Soap is partially soluble. Beeswax, African beeswax.

II. Wax deposited from chloroform solution on cooling.

(A.) Alcoholic lead acetate gives a cloudiness on standing with alcoholic solution of wax. *Wax from shellac.*

(B.) Alcoholic lead acetate gives no cloudiness.

(a.) Ethereal solution of wax becomes cloudy on addition of alcohol. *Brazilian and Curupauba wax.*

(b.) Ethereal solution remains clear. *Bahia wax.*

L. T. O'S.

**Tests for Alkaloids.** By T. TATERSALL (*Chem. News*, 41, 63).—*Delphinine*.—Thoroughly mix a small quantity with 2—3 parts of malic acid, add 6 drops pure concentrated sulphuric acid, and stir with a small agate pestle; an average red colour is produced, changing to rose red, becoming dark rose, with a violet shade at the edges after some hours, then bluish-violet, and finally "a dirty cobalt."

*Morphine*.—Concentrated sulphuric acid with a crystal of sodium arsenate gives a dim violet colour, changing to sea-green, with escape of acid vapour on heating.

M. M. P. M.

**Determination of the Alkaloids.** By J. O. TRESH (*Pharm. J. Trans.* [3], 10, 809—814).—A solution of potassium bismuth iodide may be used to estimate volumetrically solutions of the alkaloids. 4.68 grams bismuth oxide are dissolved in 80 c.c. hydrochloric acid, (B. P.); the solution is made up to 300 c.c. with water; 20 grams of potassium iodide are dissolved in 700 c.c. water; and the two solutions are mixed. By this method a clear bright orange-coloured liquid is obtained. The solution is added to the alkaloid solution from a burette until a drop of the reagent ceases to give a distinct immediate precipitate with a drop of the filtered solution. The results are not affected by the presence of hydrochloric or nitric acid, but acetic acid

decolorises the bismuth solution; this is prevented by adding a little potassium iodide to the solution of the alkaloid. Different formulæ for the precipitates were found for solutions containing varying quantities of bismuth. With a solution of the above strength the following formulæ were obtained:—

For the cinchona alkaloids the ratio of bismuth to alkaloid is 3 : 2, giving the formula  $3(\text{BiI}_3) \cdot 2(\text{Alk.HI})$ .

For the opium alkaloids the ratio is unity, giving the formula  $(\text{BiI}_3) \cdot (\text{Alk.HI})$ .

For strychnine the ratio is  $\frac{5}{6}$  formula  $5(\text{BiI}_3)6(\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_5\text{HI})$ .

„ brucine „  $\frac{9}{10}$  „  $9(\text{BiI}_3)10(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4\text{HI})$ .

„ atropine „  $\frac{1}{1}$  „  $(\text{BiI}_3)(\text{C}_{17}\text{H}_{23}\text{NO}_3\text{HI})$ .

„ aconitine „  $\frac{3}{2}$  „  $3(\text{BiI}_3)2(\text{C}_{34}\text{H}_{46}\text{NO}_6\text{HI})$ .

„ emetine „  $\frac{3}{2}$  „  $3(\text{BiI}_3)2(\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}_8\text{HI})$ .

The method may be applied to the valuation of cinchona and various other barks, and of various preparations of the alkaloids. The reaction is very delicate, the following quantities being readily detected:—

|                    |              |
|--------------------|--------------|
| Quinine .....      | 1 in 200,000 |
| Strychnine .....   | 1 „ 250,000  |
| Cinchonidine ..... | 1 „ 125,000  |
| Morphine.....      | 1 „ 20,000   |
| Atropine .....     | 1 „ 25,000   |
| Brucine .....      | 1 „ 40,000   |
| Quinidine .....    | 1 „ 150,000  |
| Aconitine .....    | 1 „ 40,000   |
| Codeine .....      | 1 „ 17,500   |
| Apomorphine.....   | 1 „ 12,500   |
| Narcotine .....    | 1 „ 50,000   |
| Narceine .....     | 1 „ 20,000   |
| Beberine .....     | 1 „ 6,000    |
| Theine .....       | 1 „ 4,000    |
| Caffeine .....     | 1 „ 3,000    |

In the case of the two last alkaloids the precipitate only forms after standing.  
L. T. O'S.

**Estimation of Amido-compounds.** By KERN (*Landw. Versuchs.-Stat*, 24, 365—373).—The apparatus used was a modification of Sachsse's, its chief advantage lying in the shortness of time required for the absorption of the nitric oxide, and the small quantity of ferrous sulphate necessary. During some experiments on asparagin it was found that the presence of ammonia salts interferes with the accuracy of the method, as they are partially decomposed by nitrous acid. It was also observed that organic acids in a high state of dilution are able to decompose amido-compounds, such as asparagin, with separation of ammonia: hence the sap of vetches, hay, &c., after being heated, will be found to contain salts of ammonia.  
J. K. C.

**Estimation of Albuminoïds and Non-Albuminoïdal Nitrogen-compounds in various kinds of Fodder.** By E. SCHULZE (*Landw.*

*Versuchs.-Stat.*, 24, 358—365). After giving a historical sketch of the discovery in vegetable products of nitrogenous bodies different from albumin, and included in the groups of amido-acids, acid amides, and peptones, the author proceeds to say that the distribution of the total nitrogen of a fodder under examination, amongst the various groups may be ascertained with sufficient exactness. The albumin is first removed by means of a lead salt, and then the peptones are precipitated by phosphotungstic acid, the amido-compounds being finally determined in the filtrate, according to Sachsse's method.

J. K. C.

**Xanthic Acid as a Precipitant for Albumin.** By P. ZÖLLER (*Ber.*, 13, 1062—1064).—Albumin, even when present in very minute quantities, is precipitated in the form of flocks when a few drops of potassium xanthate are added to the slightly acidified solution. It is better to avoid shaking the liquid, and the precipitate must consist of flocks, as xanthic acid itself renders the liquid turbid, and also precipitates some other organic substances. It is better to place the mixture in a glass dish, and allow the whole to remain at rest at a temperature of 35—38°.

In consequence of its behaviour towards albuminous substances xanthic acid acts as a powerful antiseptic.

T. C.

## Technical Chemistry.

**Rapid Developer for Wet Plate Photographs.** By J. M. EDER (*Dingl. polyt. J.*, 236, 406—409).—The author mentions the different developing solutions which have been proposed at various times. He finds that ferrous sulphate with  $\frac{1}{2}$  per cent. of salicylic acid, and a trace of sulphurous acid dissolved in water, forms a rapid developer, which has recently been introduced from Paris.

J. T.

**Industrial Utilisation of Solar Heat.** By A. MOUCHOT (*Compt. rend.*, 90, 1212—1213).—By means of large mirrors the author has been able, even in the middle of winter, to utilise solar radiation for many chemical operations, such as distillation of alcohol and various essences, calcination of alum, preparation of benzoic acid, sublimation of sulphur, distillation of sulphuric acid, and carbonisation of wood in closed vessels. He has also succeeded in working a small horizontal engine with 120 revolutions per minute, at a constant pressure of 3.5 atmospheres, and a pump yielding 6 litres of water per minute, and capable of throwing a jet 12 meters.

The large solar receiver used was of the same dimensions, and constructed on the same plan as that of Tours. Neither strong winds, nor passing clouds, exercised any appreciable effect on the working of the apparatus.

C. H. B.



**Heating Powers of Coal-gas of Different Qualities.** By W. WALLACE (*Chem. News*, 41, 41).—The heating powers were compared by causing the gases burned under similar conditions to raise the temperature of equal weights of water through the same interval. The heating value of the gases examined rose or fell with the lighting value. Comparing coal with gas the author says, "a pennyworth of coal gives as much heat as a shilling's worth of gas."

M. M. P. M.

**Examination of some County Dublin Waters.** By J. FLETCHER (*Chem. News*, 41, 62).

|                                | Total solids. | Chlorine. | Hardness.*      |               | Oxygen used † |
|--------------------------------|---------------|-----------|-----------------|---------------|---------------|
|                                |               |           | Before boiling. | After boiling |               |
| Rathmines Township, unfiltered | 42.0          | 1.28      | 12°             | 8°            | 0.12          |
| " " filtered..                 | 26.0          | 1.278     | 18              | 9             | 0.10          |
| Howorth Churchyard, No. 1 ..   | 32.0          | 3.124     | 20              | 16            | 0.22          |
| " " No. 2 ..                   | 51.0          | 6.993     | 22              | 17            | 0.13          |
| " Forge Well .....             | 70.0          | 2.378     | 17              | 16            | 0.10          |
| " Bath Well .....              | 72.0          | 3.017     | 17              | 16            | 0.10          |
| Malahide, Hotel .....          | 67.0          | 9.445     | 14              | 9             | 0.01          |
| " Strand Pump .....            | 90.0          | 6.465     | 18              | 18            | 0.18          |
| " Street Well .....            | 40.0          | 3.550     | 19              | 12            | 0.06          |
| Dalkey, Tobermoe Well .....    | 50.0          | 2.52      | 25              | 14            | 0.0           |
| " Lady Well .....              | 49.0          | 3.73      | 19              | 19            | 0.0           |

M. M. P. M.

**Action of Water on Zinc and Lead.** By X. ROCQUES (*Bull. Soc. Chim.* [2], 33, 499—501).—Zinc tanks are often found to be corroded, and a muddy deposit settles in the tank. The action is partly chemical and partly physical. From numerous experiments the author infers—(1) That zinc, lead, and copper are attacked very slowly by ordinary water and saline solutions in general (chlorides, bicarbonates). (2.) If several metals are present, the action is much more rapid. (3.) Nitrogenous matters and ammonia increase the effect mainly by their action on the zinc. (4.) The maximum effect occurs in presence of oxygen. This is particularly the case at the surface of the reservoir, where the metal is in contact with air and water by turns.

The muddy deposits consist mainly of silicates and carbonates, with 5 per cent. of zinc oxide, and 2.01 of lead oxide in one case, and in another case, where the tank had been empty for some time, 11.56 per cent. zinc oxide, and 5.85 of lead oxide. The water from the tank was not examined. For waters charged with salts, sheet-iron tanks should be used, or at least the purest zinc, and the presence of other metals or of ammonia should be avoided.

Lead pipes gave analogous results. A white crystalline deposit from tanks connected with attacked lead pipes was mainly calcium

\* Results are stated in grains per gallon; hardness in measures of soap solution.

† The water was kept in contact with standard permanganate for three hours.

carbonate, with 0.027 per cent. of lead carbonate. In boilers fed by these tubes, the lead amounted to 0.98 per cent. with a trace of copper. Iron tubes should be substituted.

J. T.

**Report on the Treatment of Sewage.** By R. A. SMITH (*Chem. News*, 41, 50).—Analyses of effluent waters from sewage purified by various methods are given. The best purifying result is gained by irrigation when no overflowing is caused by excessively wet weather; precipitation by alum, or alum and iron salts, comes next. In wet weather this process has the advantage of being nearly independent of dilution; precipitation by lime is not so efficient as the other processes.

M. M. P. M.

**Boric Acid as a Preservative.** By H. ENDEMANN (*Chem. News*, 41, 152—153).—Fresh beef, packed with 1 per cent. of boric acid and a salt pickle of 50 per cent., remained sweet and wholesome for several months, even above 26°. Beef, previously salted, could not be preserved by boric acid. Hence the salting had removed something which was necessary for the preservation of the meat. This preservative action is found to be due to acid phosphates.

Experiments, in which equivalent quantities of other inorganic acids were substituted for boric acid, gave exactly the same results, the best results being obtained by phosphoric acid and mixtures of phosphoric and hydrochloric acids.

F. L. T.

**Ammonia from the Nitrogen of the Atmosphere and the Hydrogen of Water.** By RICKMAN and THOMPSON (*Chem. News*, 41, 155).—In all attempts to manufacture ammonia synthetically the process has hitherto been to combine the nitrogen and hydrogen at a low heat, and receive the ammonia in solution in water.

Rickman and Thompson produce ammonium chloride directly. They use simply a closed brick furnace, having the ash-pit closed to regulate the supply of air, the steam being produced by the waste heat. The deoxidising material employed is the dust of steam-coal (1s. 6d. a ton at the pits), mixed with 5—8 per cent. of common salt, no other fuel being used, except to start with. The common salt, being decomposed at a red heat in presence of nascent ammonia, forming ammonium chloride.

At the present time, with the consumption of 20 to 28 lbs. of the mixture of coal-dust and salt per hour, from 2 to 3 lbs. of ammonium chloride are formed.

On p. 195 a writer (J. H.) suggests that most of the ammonia is derived from the coal itself.

F. L. T.

**On Cement.** By R. DYCKEHOFF (*Dingl. polyt. J.*, 236, 472—480).—The author has made a series of useful experiments as to the profitable application of Portland cement to the preparation of mortar and concrete. He investigated the degree of strength of the hydraulic properties of various mortars, and the firmness of the latter both when allowed to set in moist air, and when brought into water directly

after mixing. The following table shows the results arrived at with two cements:—

| Cement. | Time of setting. | Per cent. residue when sifted with a sieve of 900 meshes. | Standards. Kilos per 1 sq. cm. | Boiled, water after | 1 part cement, 3 parts sand. Firmness of cubes. Kilos. per 1 sq. cm. |         |          |                      |         |          |
|---------|------------------|---|--------------------------------|---------------------|--|---------|----------|----------------------|---------|----------|
|         |                  |   |                                |                     | Allowed to set in the air.   |         |          | Directly into water. |         |          |
|         |                  |   |                                |                     | 24 hours.  | 1 week. | 4 weeks. | 24 hours.            | 1 week. | 4 weeks. |
| A ..    | min. 20          | 10.5  | 12.6                           | 20 min.             | 11.0   | 38.2    | 79.5     | 0.75                 | 12.8    | 30.1     |
| B ..    | 600              | 5.0   | 17.8                           | 12 hrs.             | 8.4  | 60.7    | 114.4    | 0.23                 | 17.8    | 32.1     |

As to the practical value of the experiments, the author clearly indicates that it is not profitable to throw concrete direct into water, since the firmness of the mortar is influenced considerably in such a case. Similar experiments were made with poor cement mortar, with and without the addition of fat-lime, and also with mortar made up with trass and hydraulic lime. It was found that the firmness is increased considerably by adding fat-lime, both modes of "setting" being adopted, and that the cheaper kinds of cement and lime-mortar are preferable to trass or hydraulic mortar. As to the best modes of preparing concrete, economically a large amount of practical work appears to have been undertaken by the author, who concludes that—

1. The firmness of concrete is influenced materially if, as is frequently the case, pure cement is worked up with too large a proportion of flint, instead of replacing part of it by the corresponding quantity of sand.

2. Concrete, made of cement mortar and flint in economically the best proportion, has the same firmness as cement mortar, *per se*, providing that both are "beaten down."

3. A decrease in the addition of flint beyond the proportion of 1 cement, 2 sand, and 5 flint, is not economical, since the firmness is raised but slightly, whereas the cost of preparing the concrete is increased considerably.

4. As when flint contains 35 per cent. of hollow spaces, at least twice as much flint as sand may be used; the following proportions hold good in practice with such a flint. One part cement requires twice as much flint as sand, so as to produce an economically prepared concrete with a given mortar. The firmness of the concrete will then be the same as that of the mortar used in its preparation. D. B.

**Diffusive Properties of some Preparations of Iron.** By T. REDWOOD (*Pharm. J. Trans.*, 10, 709—712).—The results of experiments made on the diffusive power of some salts of iron show that whilst the sulphates and chlorides undergo diffusion to a greater

extent and with greater rapidity than the so-called preparations used in pharmacy, nevertheless the latter, and especially those with citric acid, are not deficient in diffusive power.

The experiments on dialysed iron tend to show that it cannot be considered as an active and efficacious medicine. L. T. O'S.

**Gases from Bessemer Converters.** By A. TAMM (*Chem. Centr.*, 1879, 712).—The author's results are contained in the following table:—

| Length of operation in minutes | Time from beginning of operation at which gas was collected. | Composition of gas in 100 parts by weight. |                   |       |      |       |
|--------------------------------|--|--|-------------------|-------|------|-------|
|                                |  | O.   | CO <sub>2</sub> . | CO.   | H.   | N.    |
| (1) 6                          | 1½—2½  | 0·0  | 11·04             | 23·70 | 0·08 | 65·18 |
| (2) 6                          | 5—5½   | 0·39                                       | 6·44              | 25·49 | 0·09 | 67·59 |
| (3) 7½                         | 2—3  | 0·00                                       | 9·93              | 26·18 | 0·07 | 63·82 |
| (4) 7½                         | 3½—4½  | 0·00                                       | 7·67              | 27·68 | 0·09 | 64·56 |
| (5) 6                          | 3—4  | 0·00                                       | 8·52              | 26·55 | 0·05 | 64·88 |
| (6) 6½                         | 5½—6   | 0·00                                       | 5·00              | 26·50 | 0·07 | 68·43 |
| (7) 5½                         | 2½—3½  | 0·14                                       | 7·54              | 28·51 | 0·12 | 63·69 |
| (8) 5½                         | 4½—5½  | 0·20                                       | 5·59              | 22·88 | 0·05 | 71·28 |

| Of 100 parts of air blown in                     |  |       | O taken up by slag. | O given out by the slag. | Percentage of carbon in product before addition of Mn. |
|--|--|-------|---------------------|--------------------------|--|
| There was O in form of air and H <sub>2</sub> O. | There was found in the escaping gases. |       |                     |                          |  |
|  | C.                                     | O.    |                     |                          |  |
| (1) 23·95  | 15·52                                  | 25·42 | —                   | 1·47                     | 0·25   |
| (2) 24·01  | 14·41                                  | 22·32 | 1·69                | —                        | 0·25   |
| (3) 23·87  | 16·76                                  | 26·70 | —                   | 2·83                     | 0·06   |
| (4) 24·04  | 16·60                                  | 25·45 | —                   | 1·41                     | 0·06   |
| (5) 23·67  | 16·22                                  | 25·30 | —                   | 1·63                     | —  |
| (6) 23·82  | 14·28                                  | 21·08 | 2·74                | —                        | 0·06   |
| (7) 24·35  | 17·21                                  | 26·43 | —                   | 2·08                     | 0·06   |
| (8) 23·62  | 12·21                                  | 20·13 | 3·49                | —                        | 0·06   |

M. M. P. M.

**Some Remarks on Siemens-Martin Steel.** By S. KEEN (*Chem. News*, 41, 278).—The author desires to give a short description of the working process, and a full account of some charges. All the required materials (pig-iron, steel scrap, and ladle scrap, about 8 tons altogether), are charged at once, and no additional charges are made after

the metal has become molten, unless, on testing a sample, it is shown to be too hard. In such a case the metal is softened by adding puddled blooms (15 to 20 cwts.), or, what is quicker and cheaper, good magnetic iron ore (2 to 5 cwts.) in fine powder.

Before the casting, if soft steel is wanted,  $\frac{1}{2}$  to 1 cwt. of ferromanganese is added, and for harder steel (0.5 to 0.65 per cent. of carbon) often 3 to 10 cwts. of spiegeleisen.

The following charges give an idea of the mode of working:—

**Hard Steel.**—Charge: steel scrap, 120 cwts.; ladle scrap, 17 cwts.; pig-iron (with 12 per cent. manganese), 17 cwts.; all charged at once. Charging commenced 4.30 a.m., finished at 6 a.m. Melted and one sample taken out 8.15 a.m.; 17 cwts. puddled iron blooms charged 9 a.m.; sample hammered well, cooled, bent double; 15 cwts. pig-iron, containing 9 per cent. of manganese; charged 10.20 a.m., casting took place at 11 a.m. Analysis of the steel: carbon, 0.67; manganese, 0.40 per cent.

**Medium Steel.**—Charge: steel scrap, 135 cwts.; ladle scrap, 23 cwts.; pig-iron (with 12 per cent. manganese), 10 cwts. Charging commenced 1 p.m., finished 2.45 p.m.; melted, 0.5 cwt. ferromanganese added, and first test taken 7.40 p.m. The steel was hard. 2.5 cwts. of magnetic iron ore added at 7.55 a.m. Test taken 8.30 p.m.; sample bar bent nearly double, giving only a slight crack; 0.5 cwt. of ferromanganese added; casting, 9.15 p.m. Analysis of the steel: carbon, 0.35; manganese, 0.18 per cent.

**Soft Steel.**—Charge: steel scrap, 113 cwts.; ladle scrap, 26 cwts.; pig-iron (with 12 per cent. manganese), 6.5 cwts. Charging commenced 11 a.m., finished 12.30 p.m. Melted, and first test 6 p.m.; 2 cwts. ferromanganese added 6.30 p.m.; test bar bent double after being hardened;  $\frac{3}{4}$  cwt. ferromanganese added 7 p.m.; casting, 7.15 p.m. Analysis of the steel: carbon, 0.16; manganese, 0.14 per cent. The steel was prepared for boiler plates. F. L. T

**Contributions to the Metallurgy and Docimacy of Nickel.** By E. DONATH (*Dingl. polyt. J.*, 236, 326—336 and 480—486).—The author in the first portion of his paper gives a brief outline of the history of nickel since its discovery by Cronstedt in 1751, the particulars of which are well known to chemists.

Schweder has made a series of interesting investigations as to the chemical changes which take place in the roasting of sulphuretted nickel ores. The action of carbon, carbonic oxide, and hydrogen on the sulphide of the metals connected with the nickel roasting process, has also been investigated, the following results being obtained. The sulphides of iron and copper are not acted on by carbon, carbonic oxide, and hydrogen; the sulphides of nickel and cobalt, however, lose a large portion of their sulphur when fused with carbon and ignited in a current of hydrogen; carbonic oxide, on the contrary, is inactive. The sulphates of copper, nickel, and iron are reduced by ignition with carbon, carbonic oxide, or hydrogen. Schweder has prepared sulphide of nickel of the composition NiS by fusing nickel together with sulphur. It is known that cupric sulphide is decomposed by iron,  $\text{Cu}_2\text{S} + \text{Fe} = \text{FeS} + 2\text{Cu}$ ; nickel does not, however,

decompose it, but nickel sulphide is decomposed by copper. Wagner's proposed method of preparing a useful alloy of nickel and copper from the refined ore by smelting with soda and saltpetre has also been investigated by Schweder, who found that the most satisfactory result was obtained when a mixture of  $\text{NiS}$  and  $4\text{Cu}_2\text{S}$  was used.

Badoureaux (*Annalen*, 1877, 12, 237) in giving a description of the metallurgy of nickel, mentions that in Silesia ores and iron pyrites, with 1.20—1.49 per cent. nickel, are roasted, the product being subsequently smelted with lime, clay, slag, and coke. The stone is then broken up in small pieces, again roasted, and the roasted mass smelted with quartz. A product is thus obtained, which after separating the slag contains 28—32 per cent. nickel and cobalt, 48—52 per cent. iron and copper, and 20 per cent. sulphur, and is worked up in Silesia. The roasting processes, as carried out in a number of well known nickel localities, are described more minutely in the present paper by Badoureaux; the principle, however, appears to be the same.

According to a recent analysis, emerald-green, transparent, and strongly shining garnierite, freed from all gangue, consists of—

| $\text{SiO}_2$ . | $\text{Al}_2\text{O}_3$ . | $\text{FeO}$ . | $\text{MgO}$ . | $\text{CuO}$ . | $\text{NiO}$ . | $\text{H}_2\text{O}$ . |
|------------------|---------------------------|----------------|----------------|----------------|----------------|------------------------|
| 44.0             | 1.68                      | 0.43           | 3.45           | 1.07           | 38.61          | 10.34                  |

Gard (*ibid.*, 227, 109), Zungk (*ibid.*, 222, 94), and Boussingault (*Compt. rend.*, 86, 509), have investigated the behaviour of fused nickel towards carbon and silicon, and show that after heating nickel for some time in a cementation furnace a product is obtained which is poor in carbon. Winkler describes the preparation of large castings of nickel and cobalt and of ductile nickel. He succeeded in obtaining the latter by removing carbon and silicon from nickel by means of fusion with oxide of nickel. The metal shows a tendency to become crystalline. Meiffner prepares an alloy resembling silver, and capable of resisting the action of sulphuretted hydrogen by first fusing together a mixture of 65 parts iron, 4 parts tungsten, and granulating it; and a corresponding mixture, 23 parts nickel, with 5 aluminium, and 5 copper, adding a piece of sodium to avoid oxidation. The granulated metals are then melted together.

*Docimatical and Analytical Methods of Estimating Nickel.*—Badoureaux describes the methods generally used in Varallo, Scopello, and Dobsina (Hungary). In Varallo, 2 grams of the pulverised ore are dissolved in aqua regia, the copper is precipitated with sulphuretted hydrogen, and the filtrate evaporated to dryness; the residue is dissolved in a few drops of hydrochloric acid and precipitated with chloride of lime. The whole is then dissolved in acetic acid, and the iron is thrown down by boiling the solution. The filtrate is treated with sulphuric acid, and the nickel and cobalt precipitated galvanically by means of a Bunsen battery. In order to test the ores quantitatively, 5 grams of the sample are fused with borax, soda, and metallic arsenic, and the regulus is examined with the blowpipe in a borax bead.

In Scopello, the following blowpipe method is found to give results within 0.5 per cent. of the truth. 0.1 gram of the pulverised ore is fused with an arseniferous flux consisting of a mixture of equal parts

arsenious acid, potassium cyanide, soda, fused borax, and charcoal. The test is said to occupy only a short time. The final regulus obtained represents 61·7 per cent. of a mixture of nickel and cobalt.

Schweder describes a modification of Plattner's method of estimating nickel and cobalt in cases where the ores contain copper. He determines the latter by electrolysis, and treats a second portion of the sample according to Plattner's method, deducting from the arsenic regulus, arsenite of copper, as  $\text{Cu}_3\text{As}$ , and determining the cobalt by scorification.

Allen describes a method of estimating the New Caledonian ores and others free from sulphur and arsenic. The ore is fused with potassium bisulphate and saltpetre, and the fused mass dissolved and the solution filtered. In the filtrate the iron, aluminium, and chromium are precipitated with ammonium acetate, the precipitate is redissolved and reprecipitated. Both filtrates and their washings are brought together, evaporated, and treated with sulphuretted hydrogen. Magnesium is left in the solution; nickel and cobalt, however, are converted into insoluble sulphites, which are oxidised into the sulphates and subjected either to fusion or electrolysis.

The method proposed by Margaret Cheney and Ellen T. Richards depends on the complete solubility of nickel phosphate in acetic acid in presence of sodium phosphate, whereas ferric phosphate is insoluble in the same reagent. Dirvell proposes a new method of separating nickel and cobalt quantitatively, the results, however, are inaccurate.

D. B.

**Lead Analyses.** By E. PRIWOZNIK (*Dingl. polyt. J.*, 236, 489; and *Berg. u. hüttm. Jahrb.*, 1880, 41).—(1.) Refined soft lead, Przibram; and (2) lead from Kapnik, Hungary.

|     | S.    | Cu.    | Bi.    | Ag.   | Fe.    | Zn.  | Sb.    | Pb. (by diff.) |
|-----|-------|--------|--------|-------|--------|------|--------|----------------|
| (1) | —     | ·00096 | ·00161 | ·0019 | ·00079 | ·001 | ·00277 | 99·99097       |
| (2) | ·0028 | ·136   | ·0052  | ·0023 | ·001   | —    | 1·606  | 98·2467        |

J. T.

**Analyses of Some Hair-dyes.** By J. F. BRAGA (*Chem. News*, 41, 278—279).—Hair-dyes are of two kinds, those to darken and those to lighten the hair. The latter, in all instances, were found to be hydrogen peroxide, sold under various fancy names. The former were preparations of lead, of which the thiosulphate is about the best. A successful imitation of one was made by the author as follows:—

|                          |            |
|--------------------------|------------|
| Plumbic acetate .....    | 5·7 grams  |
| Sodium thiosulphate..... | 11·5 grams |
| Glycerol .....           | 50·0 c.c.  |
| Spirits of wine .....    | 100·0 c.c. |
| Distilled water .....    | 850·0 c.c. |

The plumbic acetate was poured into a mixture of the other constituents; it should be kept in the dark.

Another was:—

|                          |             |               |
|--------------------------|-------------|---------------|
| Plumbic oxide .....      | 17·0 grams  | } To 1 litre. |
| Glycerol.....            | 300·0 grams |               |
| Precipitated sulphur.... | 17·0 grams  |               |

A third was:—

|                          |             |               |
|--------------------------|-------------|---------------|
| Plumbic acetate .....    | 12.5 grams  | } To 1 litre. |
| Glycerol.....            | 125.0 grams |               |
| Precipitated sulphur.... | 10.0 grams  |               |

The last mentioned was a very dilute solution of lead in potassium hydrate. F. L. T.

**Influence of Superfusion on the Molecular Arrangement of Cupelled Gold.** By A. D. v. RIEMSDIJK (*Chem. News*, 41, 266—267). The author refers to his research on “flashing” (*Chem. News*, 41, 126), and then remarks that a button of cupelled gold which has flashed (i.e., has been in a state of superfusion) is malleable under the hammer, but a button of cupelled gold which has been prevented from flashing (e.g., by being placed in contact with a piece of solid gold whilst still molten), is brittle under the hammer. The cause of this non-malleability is attributed to a trace of lead or bismuth not removed by cupellation. This last trace of lead or bismuth may be removed by remelting in a new cupel, and treating with a small quantity of crystallised cupric chloride. When the reaction is finished, the gold, although it solidifies without flashing, is soft and malleable. The platinum metals prevent flashing and the consequent malleability of the gold, but not to the same extent as lead or bismuth.

F. L. T.

**Alcohol Tables.** By S. COHNÉ (*Chem. News*, 41, 57, and A. H. ALLEN, *ibid.*, 70).—To convert “overproof” and “underproof” into alcohol per cent.:—Percentage of alcohol by weight = W; density = D; percentage of alcohol by volume = V; percentage of proof spirit = P.

$$\begin{array}{ll} (1) & V = P \times 0.5706 \quad (3) \quad P = V \times 1.7525 \\ (2) & V = \frac{WD}{0.7938} \quad (4) \quad P = WD \times 2.208. \end{array}$$

M. M. P. M.

**Speyer Beer.** By HALENKE (*Bied. Centr.*, 1880, 300—301).—Mean results of analysis gave—

*Summer Beer.*

| Specific gravity. | Alcohol.     |              | Extract p. c. | Ash p. c. | Water p. c. | Original concentration of the wort. p. c. | Degree of fermentation. |
|-------------------|--------------|--------------|---------------|-----------|-------------|---|-------------------------|
|                   | Weight p. c. | Volume p. c. |               |           |             |   |                         |
| 1.018             | 4.4          | 5.5          | 7.30          | 0.25      | 88.74       | 15.30                                     | 55.2                    |

*Winter Beer.*

|       |     |     |      |      |       |       |      |
|-------|-----|-----|------|------|-------|-------|------|
| 1.018 | 3.9 | 4.9 | 6.92 | 0.25 | 89.18 | 14.37 | 52.0 |
|-------|-----|-----|------|------|-------|-------|------|

A. J. C.



**Carbonic Anhydride in Beer.** By T. LANGER and W. SCHULTZE (*Bied. Centr.*, 1880, 299–300).—The brown coloration of the potash solution which occurs in the estimation of carbonic anhydride in beer by Schwackhofer's method can be avoided by passing the gas first through concentrated sulphuric acid. All the carbonic anhydride is not expelled from the beer by five minutes' boiling, but it is necessary to continue the boiling, finally aspirating  $1\frac{1}{4}$ – $1\frac{1}{2}$  volumes of air through the apparatus until the potash-tube ceases to increase in weight. Without these modifications Schwackhofer's method gives results which are too high by 100 : 107.4.

The amount of carbonic anhydride in beer is diminished by about 0.01 per cent. of the weight of the beer, if between the limits of 0° and 5° the temperature of the beer during the after-fermentation sinks or rises 1°. For example,

|                                       |   |                       |
|---------------------------------------|---|-----------------------|
| 100 per cent. CO <sub>2</sub> at 0.4° | = | 96.4 per cent at 1.6° |
| 93.7                                  | " | 2.8                   |
| 89.5                                  | " | 4.0                   |
| 85.8                                  | " | 4.7                   |

Consequently beer contains about one-seventh less carbonic anhydride at a temperature of 4.7°, than it does at 0.4°. About 0.046 per cent. of carbonic anhydride escapes through the bung-holes of the vats of stored beer, and this quantity, apparently insignificant, is really of importance if it be considered that in a tightly-closed vat of 36 hl. the beer would be forced to dissolve about 9 hl. more of carbonic anhydride.  
A. J. C.

**Tartar and Tartaric Acid in Must and Wine.** By E. MACH and others (*Bied. Centr.*, 1880, 207–211).—The different amounts of tartar and free tartaric acid found in various samples of must led the authors to experiment on the solubility of tartar in different fluids, the results of which are detailed.

The quantity of tartar depends partly on the amount of alcohol in the wine, the more alcohol the less tartar. A large amount of free tartaric acid, sugar, or glycerol also diminishes in a small degree the quantity of tartar. The influence of malic acid is considerable, but in a contrary direction; and a wine containing much malic acid will also contain larger quantities of tartar. The influence of temperature ranks in importance next to that of the percentage of alcohol; there are complicated considerations involved, but a high temperature assists the solution of tartar.

The authors recommend a low temperature during the pressure of the grape, and give directions respecting the temperature of the cellars, they asserting that in bottled wine the amount of crust will vary according as it has been bottled in summer or winter. The authors extended their enquiries to free tartaric acid in must wine, and say that the presence of this acid is a proof that the wine has been made from grapes more or less unripe; that its disappearance shows the wine to be ripe and matured, and assigns the acid taste of wine which has really been made from ripe grapes to the milder tannic, malic, succinic, and acetic acids, and their experiments show

that fine wines do not contain more than 0.2 to 0.3 per cent. of free tartaric acid.

The absence of tartar and presence of free tartaric acid is an evidence of a plaistered wine. J. F.

**Free Tartaric Acid in Wine.** By J. NESSLER and H. WACHTER (*Bied. Centr.*, 1880, 301—302).—The presence of free tartaric acid in wine does not necessarily show an improper admixture of tartaric acid to the wine. According to Mach and Rotondi the amount of free tartaric acid in the grape increases in proportion to the degree of unripeness, so that its absence from wine can only occur under certain conditions of ripeness of the grapes employed. Although unripe grapes are frequently used in considerable quantity in wine making, yet if the ripe grapes are in excess the potash salts in them are more than sufficient to separate the free tartaric acid in the form of tartar, and this explains the fact that wine so made generally contains no free tartaric acid. A wine may be suspected of having been sophisticated if with a small amount of free acid an undue proportion of it is tartaric.

A. J. C.

**Tannin in Wine.** By I. MACAGNO (*Bied. Centr.*, 1880, 212—214).—The author undertook these experiments to settle the question as to the influence of tannin on the keeping qualities of wine. In the first series on the influence of age on the contents in tannin was examined, the specimens examined being wines of the same class:—

|                  | Alcohol,<br>vol. per cent. | Glycerol<br>per liter. | Tannin<br>per liter. |
|------------------|----------------------------|------------------------|----------------------|
| Wine of 1870.... | 12.0                       | 6.10 grams             | 0.84 gram.           |
| „ 1871....       | 11.8                       | 5.80 „                 | 0.89 „               |
| „ 1872....       | 12.0                       | 5.81 „                 | 0.85 „               |
| „ 1873....       | 12.1                       | 5.32 „                 | 1.02 „               |
| „ 1874....       | 11.9                       | 4.88 „                 | 1.14 „               |

From these figures it is evident that with increase of age the tannin decreases while the glycerol increases. He finds also that the mellow-ness of old wine is due rather to the amount of glycerol than the deficiency in tannin, and that the amount of alcohol in the wine is of more importance in view of keeping qualities than is the tannin.

Further experiments were made with samples carefully bottled, the bottles well filled and closely corked, and kept for a year:—

|       | Alcohol,<br>vol. per cent. | Tannin,<br>gram liter. | Results.                           |
|-------|----------------------------|------------------------|------------------------------------|
| A.... | 6.2                        | 2.03                   | mouldy, corrupt.                   |
| B.... | 11.5                       | 1.83                   | well preserved.                    |
| C.... | 5.9                        | 1.83                   | mouldy.                            |
| D.... | 12.4                       | 0.92                   | well preserved.                    |
| E.... | 6.2                        | 0.92                   | tolerably well-preserved sediment. |
| F.... | 12.4                       | 0.38                   | turbid, corrupt; no mould.         |
| G.... | 6.3                        | 0.38                   | completely decomposed bacteria.    |
| H.... | 13.9                       | 0.43                   | perfectly clear and good.          |

D and F with the same amount of alcohol, but different quantities of tannin, seem to point to the latter as the preserving agent, but H, with more alcohol and little tannin, was well kept; it is probable that it depends on the relative proportions of alcohol and tannin.

J. F.

**Digestive Ferment produced during Panification.** By SCHEURER-KESTNER (*Compt. rend.*, 90, 369—371).—The paper relates to comestibles, made by combining meat with farinaceous products. A mixture is made of 57 parts of flour, 5 parts of baker's yeast, and 30 parts of fresh beef, very finely minced. To this as much water is added as will form a paste of convenient consistence, which is then exposed for two or three hours to a moderate temperature. The meat dissolves completely in the paste and disappears. The paste is then baked like bread, and the product may be preserved for years without change. It may be eaten, or used for the preparation of soups, &c.

R. R.

**Malt Extract and Maltose in Beer Mash.** By W. SCHULZE (*Bied. Centr.*, 1880, 205—207).—The author examines the best conditions for the production of those substances. The most favourable temperature for promoting the saccharine fermentation is 60° C., and recent investigations have shown that the production of these bodies diminishes with increase of temperature; for example, 100 parts of extract mashed at—

|     |       |         |       |           |
|-----|-------|---------|-------|-----------|
| 62° | yield | maltose | 78·64 | per cent. |
| 65  | "     |         | 70·28 | "         |
| 70  | "     |         | 62·72 | "         |
| 75  | "     |         | 59·93 | "         |

With reference to the proper amount of mash water the author differs from the conclusions of both Otto and Mulder in believing that the yield of maltose is not injuriously affected by increased proportions of water; he has obtained the same results with amount of water from 4 up to 8 of water to 1 of malt.

His next experiments were on the length of time to be given to the mashing, and he finds that a slow working from the commencement to the sugar temperature yields more extract and more maltose than rapid working.

The circumstances which exert an influence on the extract and maltose should regulate the conduct of the mash, and whether an infusion or decoction should be employed. The decision of this question has led to a great variety of experiments, the results of which may be summed up that both methods possess advantages and disadvantages peculiar to themselves, which the brewer must choose between, according to his requirements.

J. F.

**Moisture in Malting Barley.** By W. SCHULZE (*Bied. Centr.*, 1880, 204).—These moisture determinations were made of the raw barley and kiln-dried malt in the grain, the steeped and green malt in a broken state; the grain being cut lengthwise once and crosswise

four times with a fine scissors, dried in watch glasses in an air-bath at 100° to 105°, and afterwards in a desiccator.

The following is the mean of six experiments:—

|  |       |
|--|-------|
| Raw barley, percentage moisture .....                                | 14.9  |
| Steeped malt .....   | 40.3  |
| Green malt .....   | 39.9  |
| Malt after eight hours on the upper floor of a double kiln .....     | 6.5   |
| After another eight hours on the lower floor, with the plumula ..... | 1.7   |
| Ditto, ditto, without .....  | 1.6   |
|  | J. F. |

**Adulteration of Malt Combing.** By W. RICHTER (*Bied. Centr.*, 1880, 233—234).—In consequence of the death of 18 cows, after being fed on malt combings, the author made an examination of the contents of their stomachs and found them and the combings to contain large quantities of earthy matter, chiefly loamy sand, and also injurious quantities of vegetable and mineral matter, the nature of which was not ascertained.

J. F.

**Improvements in Treatment of Yeast** (*Bied. Centr.*, 1880, 224).—This paper is an account of the process of Hassal and Hehner, patented in England. The vessel containing the yeast is gradually filled with water at the lowest possible temperature, in the proportion of three volumes of water to one of yeast; after brisk agitation the mixture is left at rest 24 hours, the water is then drawn off, fresh water put in, again agitated, milk of lime added gradually, and soda or other alkaline solution until the reaction is only slightly acid; 50 kilos. of the yeast are then mixed with 42 grams of salicylic acid, the yeast is allowed to settle, and the supernatant fluid is not removed until the yeast is required for use; a mixture is then made of either malt-flour or wheat-flour with an equal quantity of sugar; this mixture is intimately blended with the yeast in the proportion of 5 to 100 of the latter; the yeast quickly seizes upon the sugary and starchy mass and becomes very active with abundant evolution of carbonic anhydride.

J. F.

**Rye as a Material for pressed Yeast.** By M. DELBRÜCK (*Bied. Centr.*, 1880, 222—223).—Rye varies considerably in its chemical composition, especially as regards the ingredients most valuable to the maker of dried yeast—the protein matters. The writer recommends analyses by competent chemists of the grain produced in different districts, which operations he shows can be completed in a short time and the results communicated with speed to the buyer. In four samples analysed by him he finds the proportions of starch and protein were—

|               |      |      |      |      |
|---------------|------|------|------|------|
| Protein ..... | 7.3  | 7.7  | 12.0 | 8.5  |
| Starch .....  | 61.1 | 62.1 | 59.0 | 61.6 |

He formulates the rule that the less suitable the grain is for flour

production the more valuable it becomes as a material for yeast manufacture. J F.

**Investigation of Lubricating Oils.** By F. FISCHER (*Dingl. polyt. J.*, 236, 487—496).—The following oils have hitherto been used most frequently for lubricating purposes: Olive oil; rape oil frequently mixed with rock oil; vegetable and animal fats, to which graphite is sometimes added; rosin oil and paraffins. The consumption of rock oil as a lubricant seems to be increasing daily. The American mineral oils are very largely used, and are brought into commerce under the name of vulcan oil, topaz oil, star oil, &c. Breymann and Hübener in Hamburg offer for sale "valvoline," and in the south of Germany oils known as emerald oil and opal oil, are mostly used.

A lubricant may be investigated in order to determine either the addition of an inferior oil or the value of the oil for lubricating purposes. To determine the presence of rosemary oil and oil of turpentine in fatty oils, it is recommended by Burstyn (*ibid.*, 214, 300) to shake up the oil with alcohol; decant the latter, distil it and add water to the distillate, a turbidity if formed indicating the presence of the ethereal oil. Mineral oils may be determined in fatty oils by saponification with soda and extraction with ether, the latter on evaporation leaving the mineral oil in the residue. In order to determine the addition of fat in a mineral oil, it is heated with the requisite quantity of soda, and alcohol is added until saponification is completed; the alcohol is then expelled by evaporation; and the residue is taken up with water, then filtered, and acidified slightly with dilute hydrochloric acid. The fatty acids are separated, and the liquid gives on evaporation the characteristic reactions for glycerol. To distinguish drying oils from non-drying ones, Poutet treats the oil with mercury dissolved in cold nitric acid; Boudet, Wimmer and Kopp with nitric acid containing nitrous acid. Non-drying oils solidify by the conversion of the olein into an elaidin, whereas the drying oils remain unaltered.

In order to determine the addition of other oils besides those above mentioned, it has been proposed to investigate the oil as to its density. Various methods of determining the density of an oil are described in the original, the particulars of which are known to chemists. This applies also to the determinations of the melting point of solid fats recommended by some chemists as forming a criterion whereby the quality of solid fats may be judged. As to the crystallising or solidifying point of a solid oil, it is mentioned that the determination of this is useful only in special cases, and not for the detection of foreign additions. The most important point is that of ascertaining the amount of free acid present in lubricating oils, and of determining the property of the oil as regards the reduction of friction. Apparatus for the direct determination of the latter point are described by the author, and in conclusion the following table is given, illustrating the results of some investigations made by the author on a number of oils:—

|                          | Original colour.                   | Sp. gr. at 15°. | Shaken up with H <sub>2</sub> O. | Shaken up with KNO <sub>3</sub> . | Shaken up with H <sub>2</sub> SO <sub>4</sub> . | HNO <sub>3</sub> increase of temperature. | Time of "flowing out." |          |
|--------------------------|------------------------------------|-----------------|----------------------------------|-----------------------------------|---|---|------------------------|----------|
|                          |                                    |                 |                                  |                                   |   |   | At 100°.               | At 40°.  |
| Water .....              | —                                  | 1·000           | —                                | —                                 | —   | —   | 38 seconds ..          | 25 secs. |
| Rock oil, Steinwerde.... | Dark brown .....                   | 0·9401          | Colourless ..                    | Yellow .....                      | Yellow .....                                    | 5·1°                                      | Undetermined           | 1,465    |
| Do. Wietze.....          | Do. ....                           | 0·9460          | Slightly turbid.                 | Do.....                           | Do. ....  | 8·2                                       | 11,450                 | 1,175    |
| Do. Itölle, near Heide.. | Do. ....                           | 0·9895          | Colourless, clear.               | Colourless ..                     | Yellowish turbidity.                            | 12·1                                      | 4,380                  | 596      |
| Do. Oodessa .....        | Brown .....                        | 0·9089          | Do.....                          | Do. ..                            | Almost colourless.                              | 4·8                                       | 1,335                  | 202      |
| Do. Seinde.....          | Dark brown .....                   | 0·8498          | Do.....                          | Do. ..                            | Yellow .....                                    | 10·9                                      | 70                     | 43       |
| Best spindle oil .....   | Pale yellow .....                  | 0·8700          | Do.....                          | Do. ..                            | Pale yellow ..                                  | 0·7                                       | 465                    | 118      |
| Amber spindle oil ..     | Orange-yellow, green fluorescence. | 0·8698          | Do.....                          | Do. ..                            | Yellowish, oil darker.                          | 1·3                                       | 472                    | 120      |
| Best machine oil ...     | Brown, greenish-blue fluorescence. | 0·8797          | Do.....                          | Do. ..                            | Yellow, oil darker.                             | 2·7                                       | 2,685                  | 368      |
| Cylinder oil .....       | Do.....                            | 0·8904          | Do.....                          | Do. ..                            | Do.....   | 2·6                                       | 12,060                 | 1,080    |
| Lignite tar oil .....    | Brown .....                        | 0·8911          | Do.....                          | Yellow, oil dark.                 | Blackish-brown.                                 | 45·6                                      | 71                     | 42       |
| Kape oil .....           | Light yellowish-brown.             | 0·9109          | Slightly turbid.                 | Saponifies ..                     | Greenish, oil greenish-blue.                    | 2·5                                       | 615                    | 191      |
| Olive oil .....          | Pale yellow .....                  | 0·9178          | Colourless ..                    | Do. ..                            | Yellowish ..                                    | 1·6                                       | 605                    | 168      |

It is a remarkable coincidence that one liter of the water associated with the oil as it comes from the well at Oedesse contains: 3.011 NaCl, 0.460 CaCO<sub>3</sub>, 0.289 MgCO<sub>3</sub> (present as bicarbonates), traces of H<sub>2</sub>SO<sub>4</sub>, SiO<sub>2</sub>, and organic matter. The presence of sodium chloride in the water points to large supplies of oil. D. B.

**Composition of Skim-milk and Cream from De Laval's Cream Separator.** By A. VOELCKER (*Jour. Roy. Agri. Soc.*, 1880, 160).—The skim-milk obtained in three trials with the centrifugal cream-separator contained only 0.22, 0.46, and 0.31 per cent. of fat. Skim-milk obtained by the usual plan of setting in shallow pans, generally contains at least 0.75 per cent. of fat. The cream from the centrifugal separator had the following composition:—

| Water. | Albuminoids. | Fat.  | Sugar. | Ash. |
|--------|--------------|-------|--------|------|
| 66.12  | 2.69         | 27.69 | 3.03   | 0.47 |

Cream obtained by ordinary skimming seldom contains 25 per cent. of fat. R. W.

**Celluloid.** (*Chem. Centr.*, 1880, 334—336; and *Techniker*, 1879, 74).—Pyroxylin obtained by treating cellulose with a concentrated mixture of 5 parts sulphuric and 2 parts nitric acid, is well washed, dried, and incorporated with about 50 per cent. of camphor, and heated to about 150° C., under hydraulic pressure. A hard elastic mass is produced, in which the greater part of the camphor added seems to have become combined. J. T.

**Researches on the Decomposition of Certain Explosives.** By SARRAU and VIELLE (*Compt. rend.*, 90, 1112—1113).—The authors have previously investigated the nature of the decomposition of gun-cotton and nitroglycerin in closed vessels under high pressures (this *Journal*, 36, 991). Under ordinary pressures, when they do not detonate, but the substance is simply inflamed by a fuse, the products of the decomposition are very different. The following table gives the composition of the gas produced by the combustion of 1 kilo. of different explosives:—

|  | NO. | CO. | CO <sub>2</sub> | H. | N.  | CH <sub>4</sub> | Total, liters |
|--|-----|-----|-----------------|----|-----|-----------------|---------------|
| Gun-cotton .....                                 | 139 | 237 | 104             | 45 | 33  | 7               | 565           |
| Gun-cotton, with 50 per cent. potassium nitrate. | 71  | 58  | 57              | 3  | 7   | 0               | 196           |
| Gun-cotton, with 60 per cent. ammonium nitrate   | 122 | 65  | 103             | 12 | 112 | 0               | 414           |
| Nitroglycerin .....                              | 218 | 162 | 58              | 7  | 6   | 1               | 452           |

In every case, nitric oxide and carbonic oxide are produced in considerable quantities. It is therefore necessary, in mining operations, to take special care to ensure detonation. C. H. B.

## General and Physical Chemistry.

Chemical Constitution of Organic Compounds in Relation to their Refractive Power and Density. Part II. By J. W. BRÜHL (*Annalen*, 203, 1—63).—The accompanying table contains those results of the author's investigation on specific refraction which have not already appeared (*Ann.*, 200, 139, and this volume, 295). Under A are found the coefficients of refraction for a ray of infinite wave-length, calculated by Cauchy's formula. B shows the coefficient of dispersion, and  $\frac{A-1}{d}$  = the specific refraction. The determinations were made at 20°, the specific gravities were also taken at this temperature, and compared with water at 4°. The weighings were reduced to vacuo.

| Name.                               | Sp. gr. | A.      | B.      | $\frac{A-1}{d}$ . | Molecular refraction. |
|-------------------------------------|---------|---------|---------|-------------------|-----------------------|
| Ethylene chloride .....             | 1·2521  | 1·41348 | 0·44888 | 0·3446            | 34·12                 |
| Ethylidene chloride .....           | 1·1743  | 1·40453 | 0·41837 | 0·3445            | 34·10                 |
| Acetic chloride .....               | 1·1051  | 1·37752 | 0·42440 | 0·3146            | 26·82                 |
| Chloral .....                       | 1·5121  | 1·44141 | 0·49833 | 0·2919            | 43·06                 |
| Propyl alcohol .....                | 0·8044  | 1·37542 | 0·34630 | 0·4667            | 28·00                 |
| Isopropyl alcohol .....             | 0·7887  | 1·36769 | 0·33624 | 0·4·65            | 27·99                 |
| Methaldehyde .....                  | 0·8604  | 1·34482 | 0·30239 | 0·4008            | 30·46                 |
| Propyl bromide .....                | 1·3520  | 1·41985 | 0·49230 | 0·3105            | 38·20                 |
| Isopropyl bromide .....             | 1·3097  | 1·41060 | 0·49581 | 0·3137            | 38·58                 |
| Propionic chloride .....            | 1·0646  | 1·39271 | 0·42309 | 0·3689            | 34·12                 |
| Propyl iodide .....                 | 1·7427  | 1·43228 | 0·79954 | 0·2767            | 47·05                 |
| Isopropyl iodide .....              | 1·7033  | 1·47570 | 0·84042 | 0·2793            | 47·43                 |
| Butyl alcohol (normal) .....        | 0·8099  | 1·38887 | 0·35569 | 0·4790            | 35·45                 |
| Trimethylcarbinol .....             | 0·7864  | 1·37759 | 0·35065 | 0·4802            | 35·53                 |
| Butaldehyde .....                   | 0·8170  | 1·37363 | 0·36843 | 0·4574            | 32·93                 |
| Isobutaldehyde .....                | 0·7933  | 1·36253 | 0·36071 | 0·4563            | 32·89                 |
| Butyric acid .....                  | 0·9587  | 1·38713 | 0·37312 | 0·4038            | 35·54                 |
| Isobutyric acid .....               | 0·9490  | 1·38259 | 0·35971 | 0·4031            | 35·43                 |
| Butyric chloride .....              | 1·0277  | 1·39978 | 0·42343 | 0·3690            | 41·43                 |
| Isobutyric chloride .....           | 1·0174  | 1·39558 | 0·42343 | 0·3888            | 41·41                 |
| Butyl chloral .....                 | 1·3956  | 1·46111 | 0·49514 | 0·3304            | 57·99                 |
| Butyl iodide .....                  | 1·6166  | 1·47857 | 0·75193 | 0·2960            | 54·47                 |
| Isobutyl iodide .....               | 1·6056  | 1·47477 | 0·73953 | 0·2957            | 54·41                 |
| Ethyl monochloracetate ..           | 1·1535  | 1·41145 | 0·39230 | 0·3552            | 43·51                 |
| Ethyl dichloracetate .....          | 1·2821  | 1·42621 | 0·42377 | 0·3324            | 52·19                 |
| Ethyl trichloracetate .....         | 1·3326  | 1·43734 | 0·46062 | 0·3163            | 60·57                 |
| Amyl alcohol .....                  | 0·8104  | 1·39655 | 0·37010 | 0·4393            | 43·06                 |
| Ethyl carbonate .....               | 0·9762  | 1·37569 | 0·33055 | 0·3848            | 45·41                 |
| Valeric chloride .....              | 0·9837  | 1·40322 | 0·42944 | 0·4078            | 49·14                 |
| Ethyl $\alpha$ -chloropropionate .. | 1·0869  | 1·40704 | 0·39265 | 0·3745            | 51·12                 |
| Ethyl dichloropropionate ..         | 1·2461  | 1·43542 | 0·43614 | 0·3491            | 59·75                 |
| Acetal .....                        | 0·8314  | 1·37217 | 0·33758 | 0·4476            | 52·82                 |
| Paraldehyde .....                   | 0·9943  | 1·39523 | 0·33456 | 0·3976            | 52·43                 |
| Ethyl acetoacetate .....            | 1·0256  | 1·40725 | 0·42910 | 0·3971            | 51·62                 |



| Name.                     | Sp. gr. | A.      | B.      | $\frac{A-1}{d}$ . | Molecular refraction. |
|---------------------------|---------|---------|---------|-------------------|-----------------------|
| Ethyl oxalate.....        | 1·0793  | 1·39920 | 0·38988 | 0·3699            | 54·00                 |
| Ethyl chlorobutyrate..... | 1·0517  | 1·41296 | 0·40829 | 0·3927            | 59·10                 |
| Oenanthal.....            | 0·8495  | 1·41426 | 0·39390 | 0·4877            | 55·59                 |
| Methylhexylcarbinol.....  | 0·8193  | 1·41325 | 0·39088 | 0·5044            | 65·57                 |
| Methylhexylketone.....    | 0·8185  | 1·40174 | 0·39524 | 0·4945            | 63·29                 |
| Triethyl citrate.....     | 1·1369  | 1·43286 | 0·43816 | 0·3807            | 105·09                |
| Tetethyl citrate.....     | 1·1022  | 1·43498 | 0·46767 | 0·3946            | 119·97                |
| Methyl alcohol.....       | 0·7953  | 1·32143 | 0·27321 | 0·4012            | 12·93                 |
| Ethyl alcohol.....        | 0·8000  | 1·35322 | 0·31532 | 0·4415            | 20·31                 |
| Water.....                | 1·      | 1·32392 | 0·30997 | 0·3239            | 5·83                  |
| Formic acid.....          | 1·2188  | 1·36062 | 0·37250 | 0·2969            | 13·61                 |
| Acetic „.....             | 1·0495  | 1·36184 | 0·34588 | 0·3448            | 20·69                 |
| Propionic acid.....       | 0·9946  | 1·37643 | 0·35210 | 0·3785            | 28·01                 |
| Valerianic „.....         | 0·9298  | 1·39344 | 0·37751 | 0·4231            | 43·16                 |
| Caproic „.....            | 0·9237  | 1·40264 | 0·38754 | 0·4359            | 50·56                 |
| Oenanthylic acid.....     | 0·9160  | 1·41005 | 0·39557 | 0·4477            | 58·19                 |
| Methyl acetate.....       | 0·9039  | 1·35156 | 0·32702 | 0·3889            | 28·78                 |
| Ethyl formate.....        | 0·9064  | 1·35088 | 0·32836 | 0·3866            | 28·61                 |
| Ethyl acetate.....        | 0·9007  | 1·36293 | 0·33405 | 0·4029            | 35·46                 |
| Methyl butyrate.....      | 0·862   | 1·37879 | 0·35077 | 0·4227            | 43·11                 |
| Methyl valerate.....      | 0·8795  | 1·38420 | 0·36715 | 0·4368            | 50·67                 |
| Ethyl butyrate.....       | 0·8892  | 1·38580 | 0·35310 | 0·4339            | 50·33                 |
| Amyl formate.....         | 0·8302  | 1·38741 | 0·36682 | 0·4401            | 51·06                 |
| Ethyl valerate.....       | 0·8661  | 1·38659 | 0·36214 | 0·4464            | 58·03                 |
| Amyl acetate.....         | 0·8561  | 1·39312 | 0·36882 | 0·4592            | 59·70                 |
| Amyl valerate.....        | 0·8568  | 1·40089 | 0·39320 | 0·4679            | 80·48                 |
| Aldehyde.....             | 0·7799  | 1·32229 | 0·32161 | 0·4132            | 18·18                 |
| Valeral.....              | 0·7984  | 1·37749 | 0·37283 | 0·4728            | 40·66                 |
| Acetone.....              | 0·7920  | 1·31888 | 0·35612 | 0·4405            | 25·55                 |
| Ethyl ether.....          | 0·7157  | 1·34368 | 0·32067 | 0·4802            | 35·53                 |
| Acetic anhydride.....     | 1·0816  | 1·37982 | 0·36614 | 0·3512            | 35·82                 |
| Glycol.....               | 1·1072  | 1·41651 | 0·37352 | 0·3763            | 23·32                 |
| Ethylene diacetate.....   | 1·1561  | 1·41010 | 0·39725 | 0·3547            | 51·79                 |
| Glycerol.....             | 1·2590  | 1·46118 | 0·40728 | 0·3663            | 33·70                 |
| Lactic acid.....          | 1·2403  | 1·42968 | 0·40794 | 0·3464            | 31·18                 |
| Phenol.....               | 1·0702  | 1·52035 | 1·03925 | 0·4362            | 45·71                 |
| Benzaldehyde.....         | 1·0455  | 1·50940 | 1·23201 | 0·4872            | 51·65                 |
| Salicylaldehyde.....      | 1·1671  | 1·52167 | 1·85280 | 0·4470            | 54·53                 |
| Methylsalicylic acid..... | 1·1801  | 1·50148 | 1·23687 | 0·4249            | 64·59                 |
| Methyl benzoate.....      | 1·0862  | 1·48961 | 0·94663 | 0·4508            | 61·30                 |
| Ethyl benzoate.....       | 1·0473  | 1·48051 | 0·88444 | 0·4588            | 63·82                 |

The following conclusions have been deduced from these observations:—

1. The atomic refraction of oxygen is variable: in those compounds in which the oxygen is attached to a carbon-atom by double linking, the value is 3·29, but in hydroxyl and in all cases where the oxygen is united to two other atoms, the atomic refraction is 2·71.

2. The atomic refraction of chlorine, bromine, and iodine, is invariable.

3. The influence of double linking of carbon with oxygen atoms is totally different from that between carbon-atoms alone. In the latter case the refractive and dispersive power is greatly increased, whilst

the double linking of carbon with oxygen exerts only a slight influence in this respect.

W. C. W.

**Atmospheric Electricity.** By MASCART (*Compt. rend.*, 91, 158—161).—The author's observations were made by means of a Thompson's quadrant electrometer, the needle of which was arranged to mechanically record its position. The pairs of quadrants were connected with the poles of a battery, the intermediate part of which communicated with the ground, while the needle was joined to a carefully insulated vessel, from which issued a stream of water. The results show that the potential of the atmosphere, always positive, is much higher and more uniform in the night than in the day. The minimum occurs at 3 p.m., and the maximum about 9 p.m., remaining nearly constant until 3 a.m.

R. R.

**Alternating Currents, and the Electromotive Force of the Electric Arc.** By J. JOUBERT (*Compt. rend.*, 91, 161—164).—The intensity of the alternating currents generated by a Siemens or a Gramme machine, are represented by a curve which is almost exactly a *sinusoid*, except that the maximum is slightly displaced in the direction of the motion. The whole curve shows, however, a retardation of one-eighth of a period, and this the author attributes to the inductive action of the current on itself.

The difference of the potential between the two carbons of the arc rises in an inappreciable time from zero to 40 or 45 volts, and its fall is rapid, but traceable. Not only does the difference of potential remain constant during the whole period of a current of given mean intensity, but even when the mean intensity of the current varies within wide limits. The author attributes to the carbons an independent electromotive force analogous to the polarisation of electrodes, but offers no explanation on this point at present.

R. R.

**A New Air Thermometer.** By A. WIRZ (*Compt. rend.*, 91, 164). The author proposes to employ Leslie's differential air thermometer for the determination of temperatures absolutely, by keeping one of the bulbs at a fixed temperature. This is accomplished by enclosing in it a coiled platinum wire, through which the current of a constant battery circulates until the circuit is broken by the movement of a column of mercury dependent upon the expansion of alcohol determined by the temperature of the air-bulb. The oscillations of temperature do not exceed  $0.1^{\circ}$ , and with only a little attention to keep in action two small Poggendorff cells, the author has kept the bulb at a uniform temperature for an indefinite number of days. By suppressing the thermoscopic bulb, the apparatus becomes a barometer, and may be employed for automatically registering the atmospheric pressure. The author proposes to call this instrument a *thermobarograph*.

R. R.

**Specific Heat and Expansion of the Solid Elements.** By H. F. WIEBE (*Ber.*, 13, 1258—1263).—In certain groups of elements, a simple relation exists (according to the author) between the pro-

ducts of the specific heat of the elements by their melting points calculated from the absolute zero.

These numbers are, for Group I: Li 8.54, Na 2.55, K 1.56, Cu 9.14, Ag 5.14, Au 3.14. II: Zn 2.33, Cd 1.33. III: Br 1.23, I 1.21, &c.

When  $\alpha$  represents the cubical expansion of a solid element,  $a$  its atomic weight,  $c$  its specific heat, and  $m$  = its melting point calculated from the absolute zero, then  $\frac{1}{\frac{a \cdot \alpha}{c \cdot m}}$  gives the constant 2.6 with a

possible error of  $\pm 0.04$ . The expansion of an element can be calculated approximately by means of the formula  $\alpha = \frac{1}{2.6 a \cdot c \cdot m}$ . Only those elements which crystallise in the regular system follow this rule. W. C. W.

**Expansion and Molecular Volumes of Liquid Organic Compounds.** By H. F. WIEBE (*Ber.*, 13, 1263—1265).—For the acids and ethereal salts of the acetic acid series, the product of the molecular weight of any of these bodies, by the mean coefficient of expansion, multiplied by the absolute boiling point, and divided by the density at  $0^\circ$ , is equal to a constant (which varies from 3.1 to 3.8) multiplied by the number of atoms in the compound,  $\frac{A\alpha}{d} T = n \text{ constant}$ , e.g., for formic acid,  $\frac{A\alpha}{d} T = 15.57 = 5 \times 3.1$ .

The density of a liquid at its boiling point  $\delta$ , can be calculated by means of the formula  $\delta = \frac{A}{2(n+1) \cdot 3.542}$ . W. C. W.

**Refrigerating Mixtures with two Crystallised Salts.** By A. DITTE (*Compt. rend.*, 90, 1282—1285).—The author has already shown that the reduction of temperature which accompanies the mixing of certain crystallised salts with concentrated acids, is to be attributed to the liquefaction of the water which separates from the hydrated salt. Such being the case, it ought to be possible to prepare refrigerating mixtures by means of two solid substances, one of which is a strongly hydrated salt; it would be necessary to effect a double decomposition of such a nature that the heat produced was very small as compared with the number of heat units absorbed in the liquefaction of the water of crystallisation.

*Ammonium nitrate and Sodium sulphate.*—Without reckoning the 10 molecules of water of the sulphate which take no part in the decomposition, the heat-units before reaction will be  $80.7 + (163.2 + 2.3) = 246.2$ , and after reaction  $157.2 + 88.9 = 246.1$ : the double decomposition will therefore be effected without sensible variation of heat, but as the 10 molecules of water set free will require for liquefaction a large number of units, it is certain that the reaction will be accompanied by a very considerable reduction of temperature. A direct experiment showed that the temperature was lowered about  $20^\circ$ ; the solution of the new products in the water formed will also tend to reduce the temperature.

In like manner, a mixture of ammonium nitrate and crystallised sodium phosphate, reacting on the same principles, effects a reduction of about  $18^{\circ}$ , and ammonium nitrate or chloride with sodium carbonate about  $25^{\circ}$ . Ammonium nitrate and dry potassium carbonate also acts as a refrigerating mixture, but the cold produced in this instance is due to the dissociation of the ammonium carbonate (Berthelot). J. W.

**Heat of Combustion of Sulphur.** By J. THOMSEN (*Ber.*, 13, 959—961).—Favre and Silbermann found the heat of combustion for one atom of sulphur, burning to form sulphurous anhydride, to be 71040 c. (*Ann. Chim. Phys.* [3], 34, 448). Berthelot (*Compt. rend.*, 84, 674), however, finds it to be 69140 c., explaining the difference of this result from that of Favre and Silbermann, by supposing that in the former case a larger amount of sulphuric anhydride was formed than in the latter. The author has determined this quantity, estimating the amounts of sulphurous and sulphuric anhydrides formed, and after deducting the heat necessary to oxidise the sulphurous anhydride to sulphuric anhydride, finds that the heat of combustion of rhombic sulphur when burning to form sulphurous anhydride, is 71080 c., and of monoclinic sulphur 71720 c.; a result agreeing with that of Favre and Silbermann. P. P. B.

**Thermochemical Investigation of the Theory of the Carbon Compounds.** By J. THOMSEN (*Ber.*, 13, 1321—1334).—The author has determined the heat of combustion and of formation of the oxides of carbon and of several hydrocarbons.

| Heat of formation.                  |                     |                          |                      |             |
|-------------------------------------|---------------------|--------------------------|----------------------|-------------|
|                                     | Heat of combustion. | Under constant pressure. | For constant volume. |             |
|                                     |                     |                          | Experiment.          | Calculated. |
| CH <sub>4</sub> .....               | 213530              | 20150                    | 19570                | 19380       |
| C <sub>2</sub> H <sub>6</sub> ..... | 373330              | 26570                    | 24510                | 24190       |
| C <sub>3</sub> H <sub>8</sub> ..... | 533500              | 30820                    | 29950                | 29000       |
| C <sub>2</sub> H <sub>4</sub> ..... | 334808              | — 4160                   | — 4740               | — 4950      |
| C <sub>2</sub> H <sub>2</sub> ..... | 495200              | + 760                    | — 400                | — 140       |
| C <sub>2</sub> H <sub>2</sub> ..... | 310570              | —48290                   | —48290               | —48660      |
| C + O ....                          | —                   | +28590                   | +28880               | +28980      |
| CO + O ....                         | —                   | +68370                   | +68080               | —           |
| C + O <sub>2</sub> ....             | —                   | +96960                   | +96960               | 96860       |

The results in column five are calculated by means of the formula  $(C_nH_{2m}) = -nd + mq + \Sigma v$ , where  $\Sigma v$  = the sum of the values of the bonds uniting the carbon-atoms together.

$d$  = the heat of dissociation of an atom of carbon = 38900 +  $x$ , and  $q = r + \frac{x}{4}$ .

$$r = 14570^{\circ}. \quad v' = r + \frac{x}{2} : v^3 = r + x : v^3 = 0 + \frac{3}{2}x :$$

$$v^4 = -2r + 2x, \text{ and } CO = 67880.$$

W. C. W

**Heat of Combustion of the Principal Gaseous Hydrocarbons.**  
By BERTHELOT (*Compt. rend.*, 90, 1240—1246).—In order to measure the heat of combustion, the hydrocarbon was exploded with oxygen in a small steel calorimeter, platinised on the interior. The numbers represent the heat of combustion at constant pressure, calculated from the determinations at constant volume:—

|                     | Heat of combustion. | Heat of formation. |                        |
|---------------------|---------------------|--------------------|------------------------|
|                     |                     | From diamond.      | From amorphous carbon. |
| Hydrogen .....      | 69.0                | —                  | —                      |
| Carbonic oxide .... | 68.3                | + 25.7             | + 28.7                 |
| Cyanogen .....      | 262.5               | — 74.5             | — 68.5                 |
| Methane.....        | 213.5               | + 18.5             | + 21.5                 |
| Ethane .....        | 388.8               | + 6.5              | + 12.5                 |
| Ethylene .....      | 341.4               | — 15.4             | — 9.4                  |
| Acetylene .....     | 318.1               | — 60.4             | — 54.6                 |
| Methyl ether.....   | 344.2               | + 50.8             | + 56.8                 |
| Propane.....        | 553.5               | + 4.5              | + 13.5                 |
| Propylene .....     | 507.3               | — 18.3             | — 9.3                  |
| Allylene.....       | 466.5               | — 46.5             | — 37.5                 |

These numbers show that the heat of combustion of a hydrocarbon is not always equal to that of its elements. The variation is least in the case of the saturated hydrocarbons,  $C_nH_{2n+2}$ , but the heat disengaged in the formation of marsh-gas from its elements appears to be greater than that of any of its homologues; a character which is in accordance with its relative stability. The difference in the cases of ethane and propane is small and nearly identical, so that if this figure remains constant for the higher homologues, we may conclude without going beyond the limits of experimental error, that the heat of combustion of the higher members of the series at least is nearly if not exactly identical with that of their elements.

The heat of formation of the other hydrocarbons is negative, the variation increasing according as the hydrocarbon is less hydrogenised; thus the addition of  $H_2$  to the formula of acetylene disengages + 45 units; to allylene, + 28.2 units, the special character of the homologous series being more marked in its first term, agreeably with what has been already mentioned in the case of marsh-gas. The addition of  $H_2$  to the formula of ethylene disengages + 21.9 units; to propylene, + 22.8, or nearly the same figure. Between any two consecutive homologues, the differences of the heat of combustion are: in the  $C_nH_{2n+2}$  series, 175.3 and 164.7; in the  $C_nH_{2n}$  series, 165.9; in the  $C_nH_{2n-2}$  series, 148.4, the actual combustion of C (diamond) +  $H_2$  being 163.

Although the calculation of the heats of formation of organic compounds by means of their combustion equivalents is accurate in principle, it must be employed with increasing reservation when the relation of the heat of combustion to the molecular weight becomes more and more considerable. Nothing can be deduced from a difference of from 3 to 4 units in the ethyl series; from 5 to 6 units in

the propyl series; nor from 8 to 10 units in the amyl series, and so on.  
J. W.

**Heat Disengaged in the Combustion of some Isomeric Fatty Alcohols, and of Oenanthal.** By W. LOUGUINIE (*Compt. rend.*, 90, 1279—1282).—The experiments of Berthelot on the formation of isomerides having similar chemical functions, led him to conclude that their formation is attended with a disengagement of nearly equal amounts of heat: the experiments of the author confirm this view.

Thus the molecule of normal propyl alcohol (taken in grams) evolved 480·3 units; of isopropyl alcohol, 478·2 units; the heat of combustion of the normal alcohol calculated theoretically by Favre and Silbermann, should be 481·2 units.

In like manner the molecule of isobutyl alcohol evolved 636·7 units; the theoretical number calculated by Favre and Silbermann being 633·6 units.

Fermentation amyl alcohol, which is a mixture of several primary alcohols, was compared against the tertiary alcohol, dimethyl-ethyl-carbinol; the former gave 793·6, and the latter 788·5 units. Favre and Silbermann's calculation for an isoamyl alcohol is 788·3 units. From these data it would follow that the different operations involved in the transformation of a primary into a secondary or tertiary alcohol, produce a calorific effect whose sum is equal to zero; the conclusion, however, holds good only on the supposition that the value of the total heats of vapourisation of the different alcohols is in all cases the same.

The molecule of oenanthal (in grams) evolved 1062·5 units of heat. From Favre's table the heat of combustion of oenanthylic alcohol should be 37·0 units higher than that of its aldehyde, or 1099·6 units; this number is less than that which corresponds to the difference, 54·0 units, between isopropyl alcohol and acetone.  
J. W.

**Thermo-chemistry of Ethylamine and of Trimethylamine.** By BERTHELOT (*Compt. rend.*, 91, 139—145).—The heat of combustion of ethylamine,  $C_2H_7N$ , is 400·7 units; that of trimethylamine,  $C_3H_9N$ , is 592·0 units. The heat of solution in water of the gas is, for ethylamine, 12·91 units; for trimethylamine, 12·90 units. Both bases have, therefore, great affinity for water, and the heat developed in diluting solutions of trimethylamine is double of that developed by equivalent solutions of potash and soda. The heats of formation of the hydrochloride, acetate, and sulphate of trimethylamine are respectively 8·9, 8·3, and 10·9 units, the substances being in solution; the formation of the solid hydrochloride from the gases gives 39·8 units. Hydrochloric acid in a solution containing equivalent quantities of trimethylamine and ammonia is nearly equally divided between the two bases.  
R. R.

## Inorganic Chemistry.

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**Vapour-density of Iodine.** By V. MEYER (*Ber.*, 13, 1010—1011). By employing a higher temperature than hitherto attained, the author finds the vapour-density of iodine to be 4.55, agreeing very nearly with the value for I, and not  $\frac{3}{2}I_2$ , as obtained at lower temperatures. The author thinks that by using still higher temperatures the iodine vapour may undergo a still further dissociation.  
P. P. B.

**Vapour-density of Iodine.** By J. M. CRAFTS (*Ber.*, 13, 1316—1321).—A reply to Victor Meyer (*Ber.*, 13, 1010 and 1103).  
W. C. W.

**Proportion of Carbonic Anhydride in the Air: Reply to a Note by M. Reiset.** By MARIÉ DAVY (*Compt. rend.*, 90, 1287—1289).—Reiset considers in the first place, that the author's results cannot be considered as accurate, because the daily volume of air used was not corrected for temperature and pressure; secondly, having made a series of experiments near Dieppe, he concludes that the proportion of carbonic anhydride in the atmosphere is practically invariable, in opposition to Marié Davy, who from experiments near Paris had found that it did vary, and had endeavoured to predict meteorological phenomena therefrom.

To this the author replies, that whereas in Reiset's experiments by weight, it was necessary to correct for temperature and pressure, in his own experiments by volume it was less important, since it only affected the third place of decimals, which was the limit of precision to which the analyses could attain.

That to deduce a perfect uniformity of composition from two series of experiments only made at an interval of six years is impossible, and that had Reiset obtained varying results instead of identical ones, it would have been equally impossible to infer a permanent change in the proportion of carbonic anhydride in the air.

To the theory of uniformity of proportion, numerous well-authenticated facts can be opposed. Truchot found 3.13 parts of carbonic anhydride in 10,000 at Clermont Ferrand, at an altitude of 395 metres; 2.03 parts at the summit of the Puy de Dôme, 1,446 metres; 1.72 parts at the summit of the Pic de Sancy, 1,884 metres; moreover, Regnault has shown that the proportion of oxygen can in certain cases, especially in warm climates, vary from 2,093 parts in 10,000 to 2,030 parts; if all the oxygen which has disappeared were to be replaced by carbonic anhydride, the proportion of this latter would rise from 3.0 parts to 66.0 parts, a variation which no one presumes ever to have observed.

During two rainy years, when Paris was under the influence of an equatorial current, a large proportion of carbonic anhydride was found. A year later, when a different atmospheric circulation obtained, a much smaller percentage of carbonic anhydride was present. Towards the end of October, 1879, the proportion of carbonic anhydride had fallen to a minimum; it was therefore concluded that a dry period was im-

minent. This coincidence was realised, and although this is at present almost the only meteorological phenomenon known to be in any way connected with the carbonic anhydride in the atmosphere, the author thinks the further prosecution of the subject is not unworthy of the attention of meteorologists.

J. W.

**Crystallised Hydrofluosilicic Acid.** By M. KESSLER (*Compt. rend.*, 90, 1285—1286).—In order to prepare a concentrated solution of hydrofluosilicic acid, silicon fluoride was passed into hydrofluoric acid. The process was very successful, and it was found that when the hydrofluoric acid was concentrated there was no deposition of silica, or absorption of excess of gas. In operating in this manner, the tube through which the silicon fluoride passed and the recipient became filled with needle-shaped crystals, which on examination proved to be a definite hydrate of hydrofluosilicic acid. They were free from hydrofluoric acid, for their aqueous solution after precipitation by excess of potassium chloride, did not corrode glass, neither did they contain excess of silicon fluoride, for the potassium silicofluoride so formed after having been washed with dilute alcohol, left behind no trace of silica in the evaporated washing waters.

The crystallised acid is colourless, very hard, and very deliquescent; it fumes strongly in the air, and melts at about  $19^{\circ}$ . Heated beyond this point it boils, but decomposes at the same time. Its composition, which was not very definitely made out, appears to be nearly  $\text{SiF}_4 \cdot 2\text{HF} + 2\text{H}_2\text{O}$ , or a little less than 2.5 molecules of water to one of acid.

The author proposes to see whether it is not possible to obtain a similar hydrate of hydrofluoric acid, or compounds of silicon fluoride with other hydracids, such as hydrobromic and hydriodic acids.

J. W.

**Pentahydrated Calcium Carbonate.** By E. PFEIFFER (*Arch. Pharm.* [2], 15, 212—216).—This compound, already described in Gmelin's Handbook from the observations of Pelouze and Salm-Hortsmar, was found by the author as a crystalline deposit in the pumps and pipes which delivered water from a well. The water, after depositing this salt, acquired a flat taste, and was almost free from carbonic acid. When the water was taken fresh from the well, shaking and stirring also caused it to deposit the above calcium salt. The solid residue of the water rose considerably, and consisted largely of potash when the deposit formed most largely. The author considers that the salt was formed by potash-lye leaking into the water and removing the carbonic acid from the water, the salt being then precipitated in a hydrated condition because of the low temperature ( $10$ — $12^{\circ}$  C.) of the water. It was kept under water unaltered at a temperature of  $20^{\circ}$  C., but at a slightly higher temperature the particles lost their transparency and water of crystallisation. In the air, it crumbled to powder and also lost its water. The crystals appeared to belong to the rhombic system.

F. O.

**Formation and Constitution of Bleaching Powder.** By G. LUNGE and H. SCHÄPPI (*Dingl. polyt. J.*, 237, 63—73).—The subject



has been much investigated, but there is still great difference of opinion. The present investigation deals with four questions. In all cases the solid substance is considered.

1. *The Influence of the Amount of Water present in the Lime on the preparation of Bleaching Powder.*—A commercial lime of great purity was used, having the following composition:—

|                                      |        |
|--------------------------------------|--------|
| CaO.....                             | 72.62  |
| CO <sub>2</sub> .....                | 0.51   |
| Al <sub>2</sub> O <sub>3</sub> ..... | 0.06   |
| SiO <sub>2</sub> .....               | trace  |
| H <sub>2</sub> O.....                | 27.80  |
|                                      | <hr/>  |
|                                      | 100.99 |

The lime, with variable amounts of water, exposed to dry chlorine, gave as follows:—

Water per cent.—

6.5, 13.6, 17.6, 21.6, 24, 26, 27.8, 28.2, 30.1, 31.8.

Bleaching chlorine—

9.06, 32.86, 37.38, 38.82, 40.71, 40.89, 43.13, 40.36, 38.78, 36.85.

Other experiments with incompletely dried, less dry, more moist, and still moister chlorine gave, for lime containing 24 per cent. of water, the following amounts of bleaching chlorine, viz, 42.12, 41.76, 38.24, and 37 per cent. respectively. Calcium hydrate dried at 100°, and containing 24 per cent. water, gave with dry chlorine 39.3 per cent., and with incompletely dried chlorine 41.59 per cent.; whilst undried hydrate with 25.3 per cent. of water gave 40.6 and 40.6 per cent. with both classes of chlorine. Hence that perfectly dry hydrate does not absorb chlorine (Graham, Tschigianjanz, &c.) is erroneous, as Stahlschmidt and Kopfer had found previously; and the absorption goes on when a large excess of quicklime is present, in which case the dryness is ensured; further, the amount absorbed is greater than would be the case if the quicklime acted as dead ballast only. The strongest bleaching powder containing up to 43.42 per cent. of available chlorine can be obtained with perfectly dry chlorine. This is produced when the lime contains about 4 per cent. more water than is necessary to form hydrate. When the chlorine contains moisture, the lime used must contain correspondingly less water, so that the end-product may be the same.

2. *The Influence of Air on Bleaching Powder.*—In moist air at about 80°, much oxygen is evolved; the whole of the chlorine remains in the residue partly as chloride and partly as chlorate, thus:  $\text{CaOCl}_2 = \text{CaCl}_2 + \text{O}$  and  $6\text{CaOCl}_2 = \text{Ca}(\text{ClO}_3)_2 + 5\text{Cl}_2$ . In dry air at 100°, the air coming away contained 0.87 per cent. of oxygen, due to the bleaching powder, and 14.94 per cent. of chlorine; the residue contained 22.25 per cent. chlorine as chloride, 3.51 as chlorate, and 1.35 as available chlorine.

3. *Bleaching Powder with Carbonic Anhydride.*—Here the authors remark that the conclusion cannot be avoided that no formula of bleaching powder can be correct in which calcium chloride appears,

since in the presence of a little moisture almost all the chlorine is expelled by carbonic anhydride. They condemn the formulæ of Gay-Lussac, Kolb, Stahlschmidt, and others as impossible, and support Odling's  $\text{Cl}-\text{Ca}-\text{OCl}$  as being sufficient to explain all observed appearances.

4. *Behaviour of the Water contained in Bleaching Powder.*—The authors conclude that the water expelled below  $150^\circ$  is either hygroscopic, or from a hydrate of  $\text{CaOCl}_2$ , or from both; between  $150^\circ$  and  $290^\circ$  very little comes off, whilst the water expelled between  $290^\circ$  and a red heat comes from free calcium hydrate. The strongest bleaching powder contains very little water in excess of what is required for the formation of  $\text{CaOCl}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{Ca}(\text{OH})_2$ . Over sulphuric acid not only is hygroscopic water removed, but also some from the compound  $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$ , if such a compound exists. Analysis of a good laboratory sample of bleaching powder gave:—

|   |        |
|---|--------|
| CaO .....   | 39.89  |
| Available Cl .....  | 43.13  |
| Cl as $\text{CaCl}_2$ .....                               | 0.29   |
| $\text{H}_2\text{O}$ (mean of three determinations) ..... | 17.00  |
| $\text{CO}_2$ .....                                       | 0.42   |
|   | <hr/>  |
|   | 100.73 |

From which the following composition may be calculated:—

|   |        |
|---|--------|
| $\text{CaOCl}_2$ .....                    | 88.08  |
| $\text{CaCO}_3$ .....                     | 0.96   |
| $\text{CaCl}_2$ .....                     | 0.45   |
| $\text{Ca}(\text{OH})_2$ .....            | 6.74   |
| $\text{H}_2\text{O}$ (by difference) .... | 3.77   |
|   | <hr/>  |
|   | 100.00 |

Actual determination of the water gave 0.66 per cent. more. The small quantity of calcium hydrate need not be considered essential to the formula of bleaching powder, but seems due to mechanical admixture. The circumstance that good bleaching powder rubbed up with a little water swells up and evolves heat, can easily be explained by the equation  $2(\text{Cl} \cdot \text{Ca} \cdot \text{OCl}) = \text{ClO} \cdot \text{Ca} \cdot \text{OCl} + \text{CaCl}_2$ . On diluting, the resulting product is obtained as voluminous flocculent precipitate, as if separated from combination.

J. T.

**Compound of Alumina with Carbonic Anhydride and Ammonia.** By M. BARTH (*Annalen*, 202, 372—375).—Various statements have been made with regard to the composition of the precipitate produced in a solution of alum by ammonium carbonate, by Bley (*J. pr. Chem.*, 39, 1); Barratt (*ibid.*, 82, 61); Parkmann (*ibid.*, 89, 116); Muspratt (*Annalen*, 72, 120); Langlois (*ibid.*, 100, 374); Wallace (*Jahresb.*, 1858, 70); and Rose (*Pogg. Ann.*, 91, 461). Bley proved that it contained alumina, carbonic anhydride, and often ammonia; Muspratt gave it the formula  $3\text{Al}_2\text{O}_3 \cdot 2\text{CO}_2 + 16\text{H}_2\text{O}$ ; while Rose regarded it as  $\text{Al}_2\text{O}_3 + (\text{NH}_4)_2\text{O} + 2\text{CO}_2 + 4\text{H}_2\text{O}$ ; and Langlois as  $3(\text{Al}_2\text{O}_3 \cdot \text{CO}_2) + 5(\text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O})$ . Recently Urbain and Renoul

(*J. Pharm. Chim.* [4], 30, 340) regard the precipitate formed in the cold as  $\text{CO}_2 + \text{Al}_2\text{O}_3 + 8\text{H}_2\text{O}$ .

By adding a solution of pure alumina in hydrochloric acid to excess of cold ammonium carbonate, the author obtained a precipitate which, when washed with cold water and dried over oil of vitriol, contained (in one case)  $\text{Al}_2\text{O}_3 = 37.44$ ,  $\text{CO}_2 = 17.7$ ,  $\text{NH}_3 = 4.92$ , and  $\text{H}_2\text{O} = 39.94$  per cent. It was obviously a mixture of a double aluminium and ammonium carbonate, with either alumina or aluminium carbonate. A carbonate without ammonia has not as yet been proved to exist. Ch. B.

**New Aluminium Sulphate.** By P. MARGUERITE (*Compt. rend.*, 90, 1354—1357).—When ammonium alum is decomposed by heat, anhydrous aluminium sulphate is first obtained. By pushing the decomposition somewhat further, sulphuric acid is volatilised; so that by carefully regulating the heat, a residue can be finally obtained almost entirely soluble in water, and consisting mainly of the *sesquibasic* sulphate. This salt, which has not been before described, is entirely different in appearance from the ordinary sulphate. It crystallises in rhombohedrons and not in nacreous scales; its solubility in water at  $15^\circ$  is about 45 per cent., but it can be separated from the ordinary sulphate by fractional crystallisation. Analysis gave:—

| $\text{Al}_2\text{O}_3$ . | $\text{SO}_3$ . | $\text{Fe}_2\text{O}_3$ . | $\text{H}_2\text{O}$ . | Loss.      |
|---------------------------|-----------------|---------------------------|------------------------|------------|
| 21.2                      | 33.84           | 0.01                      | 44.90                  | 0.05 = 100 |

from which the formula  $\text{Al}_2\text{O}_3.2\text{SO}_3.12\text{H}_2\text{O}$  or  $\frac{2}{3}\text{Al}_2\text{O}_3.3\text{SO}_3.18\text{H}_2\text{O}$  is deduced.

A list is given in the memoir of ten different aluminium sulphates which are known at the present day. J. W.

**Specific Heat and Atomic Weight of Glucinum.** By L. F. NIXON and O. PETERSON (*Compt. rend.*, 91, 168—171).—The authors have redetermined the equivalent of glucinum, using pure specimens of glucina, the mean of four experiments being 4.542 ( $\text{O} = 8$ ). If glucina be  $\text{Gl}_2\text{O}_3$ , this gives 13.65 as the atomic weight of glucinum. They find also that the specific and atomic heats of glucinum increase with the temperature like those of iron, but at  $300^\circ$  the atomic heat of glucinum is not so great as that of iron. Glucinum cannot therefore be compared with carbon, boron, and silicon, the specific heats of which increase much more rapidly. The atomic heat of glucinum is quite normal if the atomic weight be taken as 13.65. R. R.

**Colloidal Ferric Hydrate.** By L. MAGNIER DE LA SOURCE (*Compt. rend.*, 90, 1352—1354).—Several specimens of *dialysed iron* were analysed and found to vary in composition from  $12\text{Fe}_2\text{O}_3.\text{Fe}_2\text{Cl}_6$  to  $30\text{Fe}_2\text{O}_3.\text{Fe}_2\text{Cl}_6$ . The latter preparation, known in commerce as "fer Bravais," was constant in composition, and was identical with the basic oxychloride of iron, the formula of which was first accurately ascertained by Graham.

In order to find out whether this constancy of composition was due to the impossibility of separating the whole of the ferric chloride

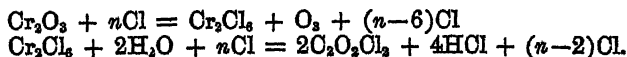
by dialysis, a sample was diluted so as to contain 0·8 per cent. of ferric oxide, and submitted to prolonged dialysis for three months. At the beginning of the experiment, the composition of the liquor was  $30\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6$ ; after one month,  $64\text{Fe}_2\text{O}_3$ ; after two months,  $102\text{Fe}_2\text{O}_3$ ; after three months,  $116\text{Fe}_2\text{O}_3$  to one molecule of  $\text{Fe}_2\text{Cl}_6$ ; whilst traces of chlorine still continued to pass through the diaphragm. The latter was now in too small proportion to measure quantitatively, but it was placed beyond doubt that the oxychloride of composition  $116\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6$ , still lost chlorine by dialysis.

The author thinks that these experiments are sufficient to prove that ferric hydrate is, under certain conditions, soluble in water, and that it is unnecessary, in order to explain such solubility, to imagine that the hydrate is engaged in some more or less complex combination. In support of this opinion, it may be mentioned that, from considerations of an altogether different character, Debray has already arrived at the same conclusion.

When "fer bravais" is evaporated to dryness and the residue treated with water, the ferric chloride dissolves, but the ferric hydrate remains insoluble; the hydrate, in solution, and dried at  $100^\circ$ , appears to be the normal salt  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , at least as far as theoretical calculation of the weight of residue from known quantities of solution may be considered to support such a conclusion. J. W.

**Action of Chlorine on Chromium Sesquioxide.** By H. MOISSAN (*Compt. rend.*, 90, 1357—1360).—Strongly ignited chromium sesquioxide submitted to the action of dry or moist chlorine at  $440^\circ$  is not attacked, but chromium sesquihydrate under similar circumstances is readily attacked, and red vapours are produced, which condense to chromium oxychloride,  $\text{Cr}_2\text{O}_2\text{Cl}_2$ .

It would appear that chromium sesquioxide, anhydrous but not calcined, is attacked by chlorine at  $440^\circ$  with production of the sesquichloride and not of the oxychloride, but the action soon ceases, owing to the superficial coating of sesquichloride preventing the further action of chlorine; the presence, however, of water either in the current of chlorine or in the oxide brings about at this temperature the decomposition of the sesquichloride, according to the following equations:—



If the passage of moist chlorine over the non-calcined sesquioxide be stopped as soon as red vapours begin to be disengaged, and the excess of chlorine be expelled by a current of carbonic anhydride, there will be found to remain in the apparatus a brown powder, the composition of which is nearly that of the oxychloride of Moberg. It is an intermediate substance less oxidised than the ordinary oxychloride, and decomposable by water. Chromium oxychloride also results from the action of dry oxygen at  $440^\circ$  on the sesquichloride. With the non-calcined sesquioxide, oxygen causes an increase in weight, and a blackish-grey substance is produced which seems to be the oxide

$\text{CrO}_2$ ; it evolves chlorine readily when treated with concentrated hydrochloric acid. J. W.

**Combinations of Uranium Oxyfluo-Compounds with Fluorides of the Alkali Metals.** By A. DITTE (*Compt. rend.*, 91, 166—168).—The action of the *neutral* fluoride of an alkaline metal on the green oxide of uranium gives rise to insoluble, anhydrous crystalline compounds, having the formula  $\text{U}_2\text{O}_2\text{F}_{1.4}\text{MF}$ . *Acid* fluorides of alkali metals, on the other hand, react to produce soluble hydrated salts, having the composition  $\text{U}_4\text{OF}_{1.4}\text{MF}_{1.2}\text{H}_2\text{O}$ . R. R.

## Organic Chemistry.

**Action of Ethyl Chloride on Ethylamines.** By E. DUVILLIER and A. BUISINE (*Compt. rend.*, 91, 173—175).—When ethyl chloride is heated at  $100^\circ$  in a sealed tube with an alcoholic solution of the ethylamines produced in the reaction between ethyl chloride and ammonia, and the product is treated with soda in excess, four ethyl bases are obtained, namely, triethylamine, diethylamine, monethylamine, and tetrethylammonium hydrate. R. R.

**Decomposition of Simple Organic Compounds by Zinc-dust.** By H. JAHN (*Ber.*, 13, 983—990).—The alcohols from ethyl alcohol upwards are decomposed by zinc-dust at  $300\text{--}350^\circ$  into hydrogen and the olefine corresponding with the alcohol. Propyl and isopropyl alcohol both yield a propylene whose dibromide boils at  $142\text{--}143^\circ$ . Methyl alcohol holds an exceptional position; it is decomposed into carbonic oxide, hydrogen, and a small quantity of marsh-gas. Ethyl alcohol undergoes a similar decomposition at a dull red heat, yielding marsh-gas, carbonic oxide, and hydrogen. This decomposition of methyl alcohol is, to some extent, to be accounted for by the constitution of its molecule; and, further, Berthelot (*Compt. rend.*, 54, 515) has shown that with respect to heat of formation, methyl alcohol holds an exceptional position as compared with its homologues.

P. P. B.

**Combination of Allyl Alcohol with Baryta.** By C. VINCENT and DELACHANAL (*Compt. rend.*, 90, 1360—1361).—When allyl alcohol is dried over anhydrous baryta, as is generally recommended, a very large loss of alcohol results; it was thought probable, therefore, that some combination had taken place between the baryta and the alcohol. The addition of baryta causes a very considerable development of heat, the alcohol becomes yellow, and the liquid portion when filtered from the excess of baryta and evaporated to dryness leaves a mass of microscopic crystals. From these crystals, which contain 62 per cent. of baryta, the alcohol can be recovered by distillation with water. The formula  $2\text{C}_3\text{H}_5\text{O}, \text{BaO}$  requires 56.88 per cent. of baryta, the excess of baryta found over that theoretically

required being due to the solubility of barium hydrate in the solution of the allylate. Allyl alcohol also dissolves barium allylate, and this solution when evaporated over sulphuric acid leaves an amorphous mass, which dries with difficulty at the ordinary temperature. In a vacuum at  $100^{\circ}$ , however, the allylate becomes perfectly dry, and has then acquired the property of decomposing rapidly on a slight elevation of temperature, leaving a pulverulent and very voluminous carbonaceous residue.

J. W.

**Action of Bromine on Cane-sugar.** By O. GRIESHAMMER (*Arch. Pharm.* [3], 15, 193—210).—The author gives a short notice of the researches on this subject of Hlasiwetz, Barth, and of Habermann, and then states that he has found that bromine readily acts on a warm aqueous solution of cane-sugar. When 2 atoms of bromine were added, the colour quickly vanished; on further addition of 2 atoms, the colour disappeared after several weeks; a fifth atom did not disappear after long standing, but decomposition and blackening took place, and was increased by heating the liquid. After the reaction, the bromine was found to be entirely present as hydrobromic acid, no bromo-derivative of sugar being formed. The hydrobromic acid was removed by lead oxide, since when silver oxide was used, silver was reduced. After removal of the lead by sulphuretted hydrogen and evaporation to one-half, the easily decomposed acid liquid was saturated whilst warm with zinc carbonate, and the zinc-salt was precipitated and well washed with strong alcohol. This salt is easily soluble in water, and its solution when treated with sulphuretted hydrogen yields the uncrystallisable acid. The solution was evaporated over calcium chloride, and the formula obtained for the acid was  $C_6H_{12}O_7 + 2H_2O$ ; 1 mol. of water can be expelled at  $100^{\circ}$ , and the second at  $125^{\circ}$ . A column 200 mm. in length of a 1 per cent. solution rotates the plane of polarisation  $2^{\circ}$  to the right in Mitscherlich's apparatus. The aqueous solution when made alkaline separates no cuprous oxide from Fehling's solution, thus differing from Hlasiwetz's acid, which doubtless contained sugar. Analyses of the salts of barium, calcium, zinc, silver, lead, potassium, and ammonium are given; no acid salts could be prepared. The name gluconic acid has been retained by the author, although the acid is not identical with that obtained by Hlasiwetz. The acid was separated directly from the product of the action of bromine on cane-sugar without previous treatment with lead oxide by warming with zinc carbonate until the liquid was only feebly acid, evaporating to one-half, and shaking with eight times as much 90 per cent. alcohol: the precipitate when well washed yielded pure gluconic acid. Carbonates and hydrates of the metals of the alkalis and alkaline-earths caused decomposition, and did not yield gluconates.

A study of the reaction quantitatively showed that if more than 2 atoms of bromine were employed, no increased oxidation occurred, and the main reaction is therefore probably represented thus:  $C_{12}H_{22}O_{11} + 2Br + 2H_2O = C_6H_{12}O_7 + C_6H_{12}O_6 + 2HBr$ . The gluconic acid and grape-sugar were obtained in nearly the proportions required by this equation; but a certain amount of the sugar was changed into a

gum-like substance, which was convertible into grape-sugar by being treated with dilute sulphuric acid. A fuller examination of this sugar and gum is promised. F. C.

**Presence in Soja hispida of a Substance soluble in Alcohol, and transformable into Glucose.** By A. LEVALLOIS (*Compt. rend.*, 90, 1293).—The analysis of this seed by Pellet gave 3.1 per cent. of sugar starch and dextrin. The author's results are different. He finds 9—11 per cent. of a substance soluble in alcohol, which reduces Fehling's liquor only after some minutes' boiling with water acidulated with sulphuric acid. It has considerable dextrorotatory power, which is brought back to nearly that of glucose (dextrose?) by boiling with acidulated water. In its optical characters it resembles dextrin, but seems to differ from it in the rapidity with which it is converted into glucose. J. W.

**Behaviour of the Ethyl-mercaptides of Mercury and Lead at High Temperatures.** By R. OTTO (*Ber.*, 13, 1289—1290).—When mercuric ethylmercaptide (m. p. 76°) is heated with alcohol at 180°, it splits up into metallic mercury and ethyl disulphide, only traces of mercuric sulphide being formed. A similar decomposition takes place when the dry mercaptide is heated, but in this case a somewhat larger quantity of mercuric sulphide is produced.

Lead ethylmercaptide melts at 150°, and decomposes at 180°, forming lead sulphide and ethyl sulphide. W. C. W.

**Etherification of Sulphuric Acid.** By A. VILLIERS (*Compt. rend.*, 91, 124—127).—Berthelot has already shown that in a mixture of sulphuric acid and alcohol, the proportion of acid neutralised tends towards a limit which it cannot pass, and that this limit becomes gradually lower under the influence of time and temperature, owing to the formation of ordinary ether. The following table shows the influence of time in the etherification of sulphuric acid (ethyl hydrogen sulphate being formed) at 100°:—

|                       | Percentage of acid etherified. |             |             |
|-----------------------|--------------------------------|-------------|-------------|
|                       | $C_2H_5O.$                     | $2C_2H_5O.$ | $4C_2H_5O.$ |
| Immediately .....     | 59.0                           | 74.6        | 83.2        |
| After 15 minutes .... | 58.0                           | 72.2        | —           |
| „ 2½ hours .....      | 49.3                           | 64.3        | 76.0        |
| „ 26 „ .....          | 45.5                           | 46.5        | 53.9        |
| „ 69 „ .....          | 45.5                           | 45.3        | 34.7        |
| „ 154 „ .....         | —                              | 44.1        | 32.1        |

At the end of the experiment, the proportion of sulphuric acid which remains in combination with the alcohol appears to correspond with a certain composition of the original liquor. This retrograde action is observable also at 100° with mixtures containing water; as might be expected, it is greater than when alcohol alone is used.

Percentage of acid etherified,  $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\text{O} +$ 

|                             | $\frac{1}{2}\text{H}_2\text{O}$ . | $\text{H}_2\text{O}$ . | $2\text{H}_2\text{O}$ . |
|-----------------------------|-----------------------------------|------------------------|-------------------------|
| Immediately .....           | 53.0                              | 48.4                   | 40.0                    |
| After 15 minutes ....       | 49.9                              | —                      | —                       |
| „ $2\frac{1}{2}$ hours .... | 42.7                              | 39.3                   | 34.1                    |
| „ 69 „ .....                | 38.2                              | 35.7                   | 28.0                    |
| „ 154 „ .....               | 37.0                              | 33.8                   | 27.5                    |

The formation of ether and diminution in proportion of acid half neutralised goes on even at much lower temperatures: thus at  $44^\circ$ —

Percentage of acid etherified.

|                    | $\text{C}_2\text{H}_5\text{O}$ . | $\text{C}_2\text{H}_5\text{O} + \frac{1}{2}\text{H}_2\text{O}$ . | $\text{C}_2\text{H}_5\text{O} + \text{H}_2\text{O}$ . |
|--------------------|----------------------------------|--|---|
| Immediately .....  | 59.0                             | 53.0   | 48.4  |
| After 69 days..... | 48.7                             | 42.1   | 39.4  |
| „ 142 „ .....      | 44.5                             | 37.9   | 36.0  |
| „ 221 „ .....      | 44.5                             | 37.4   | 33.6  |

These results show that the action tends towards a fixed limit at  $44^\circ$ , and that the ultimate limits corresponding to the temperatures of  $44^\circ$  and  $100^\circ$  are identical. The coefficient of etherification begins to increase at first rapidly, and passes to a maximum, which corresponds with a short period of unstable equilibrium; it then steadily diminishes, and ultimately settles to a period of stable equilibrium, which is independent of the temperature. J. W.

**Preparation of Neutral Ethyl Sulphate.** By A. VILLIERS (*Compt. rend.*, 90, 1291—1292).—This ether can be prepared by distilling in a vacuum a mixture of sulphuric acid and alcohol. 200 grams of absolute alcohol distilled *very slowly* in this manner with twice their volume of concentrated sulphuric acid, yielded from 25 to 30 grams of the neutral ether; the end of the operation is indicated by the frothing of the contents of the retort, and by an increase of the internal pressure. The distillate separates into two layers, the lower of which consists of the pure ether. There is no advantage in using fuming sulphuric acid, or in substituting ordinary ether for alcohol. The boiling point of ethyl sulphate under a pressure of 45 mm. is  $120.5^\circ$ , which falls regularly  $2.5^\circ$  as the pressure diminishes 5 mm. It solidifies at about  $-24.5^\circ$ , and when treated with warm baryta-water it gives the theoretical quantity of barium ethyl sulphate and alcohol. J. W.

**Transformation of Methyl Thiocyanate at High Temperatures.** By A. W. HOFMANN (*Ber.*, 13, 1349—1352).—When methyl thiocyanate is heated at  $180$ — $185^\circ$  for six hours, it is converted partly into a polymeric modification,  $\text{C}_6\text{H}_6\text{N}_3\text{S}_3$ , and partly into methyl thiocarbimide. The two substances are separated by distillation, the latter boiling at  $118^\circ$ , the former remaining in the retort.

The polymeride,  $\text{MeS}-\text{C} \begin{array}{c} \text{N}=\text{C}-\text{SMe} \\ \text{N}-\text{C}-\text{SMe} \end{array}$ , forms colourless crystals,



which melt at  $188^{\circ}$ , and sublime at a higher temperature. They are insoluble in dilute acids and alkalis, but dissolve in hot glacial acetic acid.

Hot hydrochloric acid splits up the compound into methyl mercaptan and cyanic acid.

A crystalline base is obtained by acting on the new methyl thiocyanate with alcoholic ammonia at  $150^{\circ}$ . W. C. W.

**Furfuraldehyde.** By E. FISCHER (*Ber.*, 13, 1334—1340).—The name *furoin* is given to a compound having the composition  $C_4H_3O.C_2H_3O_2.C_4H_3O$ , which bears the same relation to furfuraldehyde that benzoïn bears to benzaldehyde. This substance is prepared by boiling 40 parts of furfuraldehyde with 30 of alcohol, 80 of water, and 4 parts of potassium cyanide for three-quarters of an hour. The crystalline mass which is deposited on cooling is drained, washed first with water, then with a small quantity of alcohol, and dried between filter-paper. It is obtained nearly colourless by precipitation with alcohol from its solution in hot toluene. Furoin forms slender prisms (m. p.  $135^{\circ}$ ) soluble in hot water and hot toluene. It also dissolves in sulphuric acid with an intense bluish-green coloration. The acetate,  $C_{10}H_7O_4Ac$ , m. p.  $75^{\circ}$ , is with difficulty obtained in a pure and colourless state. Furoin dissolves freely in aqueous or alcoholic solutions of soda, forming a deep red liquid, which appears bluish-green by transmitted light. On passing a rapid current of air through the solution, oxidation takes place, the colour changes, and crystals of *furil*,  $C_4H_3O.C_2O_2.C_4H_3O$ , are deposited. By recrystallisation from alcohol this compound is obtained in golden needles (m. p.  $162^{\circ}$ ), soluble in chloroform and in hot alcohol.

An unstable acid appears to be formed by the action of a concentrated potash solution on furil. When such a solution is neutralised with sulphuric acid and extracted with ether, a thick oily liquid is obtained, which dissolves in alkalis and in ether. It undergoes a rapid spontaneous transformation into a black solid mass, insoluble in the usual solvents. A chloroform solution of furil is not attacked by bromine or chlorine, but when the dry compound is brought in contact with excess of pure bromine, an octobromide,  $C_{10}H_4Br_8O_4$ , is produced. The bromide is soluble in hot chloroform, but is partially decomposed by recrystallisation. The crystals change colour at  $150^{\circ}$ , and melt with decomposition at  $185^{\circ}$ , bromine and hydrobromic acid being evolved, whilst *dibromofuril*,  $C_{10}H_4Br_2O_4$ , remains. By dissolving the residue in hot alcohol and boiling with animal charcoal, the dibromofuril is obtained in golden plates (m. p.  $183^{\circ}$ ). The mother-liquor contains a yellow crystalline compound (m. p.  $110^{\circ}$ ), soluble in alcohol and ether, whose composition has not been ascertained.

**Benzofuroin**,  $Ph.CO.CH(OH).C_4H_3O$  or  $Ph.CH(OH).CO.C_4H_3O$ , is produced when a mixture of furfuraldehyde (18 parts), benzaldehyde (20), alcohol (60), water (80), and potassium cyanide (4), is boiled for 15 minutes in a flask provided with an upright condenser. After successive recrystallisations from hot water, benzene, and alcohol, the pure compound is obtained in crystals melting at  $138^{\circ}$ .

In its properties it occupies an intermediate position between benzoïn and furoïn.  
W. C. W.

**New Lactones.** By R. FITTIG (*Ber.*, 13, 955—956).—To the class of bodies styled lactones (this vol., p. 378) the following have been added. Lactone of normal caproic acid,  $C_6H_{10}O_2$ , obtained by boiling the bromocaproic acid from hydrosorbic acid with water; it is a liquid boiling at  $220^\circ$ . Lactone of normal valerianic acid,  $C_5H_8O_2$ , obtained by boiling the addition-compound of allyl acetic and hydrobromic acid with water; it is a liquid, and boils at  $206$ — $207^\circ$ . A third lactone has been obtained by the dry distillation of terpenylic acid, the homologue of terebic acid. This lactone is a liquid, containing seven atoms of carbon, and boils at  $203$ — $204^\circ$ .

The above lactones may be distilled without decomposition, are volatile in steam, and dissolve in water, forming neutral solutions, from which they may be separated by addition of alkaline carbonates as oils. When boiled with caustic alkalis they yield salts of the corresponding hydroxy-acids.  
P. P. B.

**Double Salts of the Lower Members of the Acetic Acid Series.** By A. FITZ (*Ber.*, 13, 1312—1316).—The following double salts of propionic acid were prepared:—

$Ba(C_2H_3O_2)_2 + 2Ca(C_2H_3O_2)_2$ , regular octohedrons.

$Sr(C_2H_3O_2)_2 + 2Ca(C_2H_3O_2)_2$ , resembling the preceding compound in appearance, but crystallising in a combination of the quadratric pyramid and secondary prism 1 : 1 : 0.9759.

$Pb(C_2H_3O_2)_2 + 2Ca(C_2H_3O_2)_2$  is isomorphous with the calcium strontium double salt.

$Ba(C_2H_3O_2)_2 + Mg(C_2H_3O_2)_2 + H_2O$  crystallises in a combination of the cube, dodecahedron, and tetrahedron.

$Pb(C_2H_3O_2)_2 + Mg(C_2H_3O_2)_2 + H_2O$  resembles the preceding salt.

Calcium barium butyrate crystallises in anhydrous regular octohedrons.

Sodium formate acetate,  $NaC_2H_3O_2 + NaCHO_2 + 2H_2O$ , forms monoclinic crystals,  $a : b : c = 2.101 : 1 : 0.617$ ;  $\beta = 86^\circ 21'$ .

Barium isobutyrate and acetate,  $(C_4H_7O_2)_3Ba + (C_2H_3O_2)_3Ba + H_2O$ , resembles in crystalline form the double acetate and propionate of barium.  
W. C. W.

**Dichloracrylic Acid.** By O. WALLACH (*Annalen*, 203, 83—94).—In the preparation of dichloracrylic acid by the action of nascent hydrogen on chloralide (*Ber.*, 10, 567, and this Journal, 1877, ii, 591), the formation of monochloracrylic acid can be avoided by stopping the operation before the whole of the chloranilide is decomposed. The acid  $CCl_2:CH.COOH$  melts at  $76^\circ$  and solidifies at  $59^\circ$ . By suddenly cooling the melted acid, it is converted into a modification melting at  $63^\circ$ . The addition of dilute sulphuric acid to an aqueous solution of a pure dichloracrylate throws down needle-shaped crystals of the free acid. From impure salts, the acid is precipitated as an oily liquid.

Barium dichloracrylate,  $(CCl_2:CH.COO)_2Ba + 2H_2O$ , crystallises in  
3 k 2

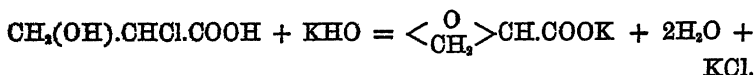
six-sided plates, probably belonging to the monoclinic system. The calcium salt forms crystals resembling those of the barium salt, and also crystallises in needles. The free acid is not attacked by water at 200°, but is decomposed by boiling baryta water, with formation of monochloroacetylene. The reaction probably takes place in two stages, chloropropionic acid being first formed, which afterwards splits up into spontaneously inflammable chloroacetylene and carbonic anhydride (*Ber.*, 11, 751; 12, 57; and this Journal, *Abst.*, 1878, 653; and 1879, 453).

These reactions show that this acid is not identical with that obtained by Bennett and Hill (*Ber.*, 12, 655, and this Journal, 1879, *Abst.*, 616) from chloromucic acid.

β-monochloroacrylic acid is not decomposed by baryta-water at 180°. W. C. W.

**Constitution of Liquid Chlorolactic Acid and of Oxyacrylic Acid.** By P. MELIKOFF (*Ber.*, 13, 956—958).—By treatment with zinc and sulphuric acid, liquid chlorolactic acid yields propionic acid and a lactic acid, which, when treated with hydriodic acid, gives crystalline β-iodopropionic acid, m. p. 82.5°. The formation of the latter shows liquid chlorolactic acid to be chlorhydracrylic acid, i.e., an α-derivative.

The formation of oxyacrylic acid from α-chlorolactic acid is similar to that of epichlorhydrin from dichloropropyl alcohol, thus:—



Oxyacrylic acid, like epichlorhydrin, unites with hydrochloric acid, yielding β-chlorolactic acid, whilst the latter yields dichlorhydrin.

Oxyacrylic acid is the inner anhydride of glyceric acid, and therefore the author styles it glycidic acid. It unites with ammonia, forming an amido-derivative. P. P. B.

**β-Bromolactic Acid.** By P. MELIKOFF (*Ber.*, 13, 958).—This compound is obtained by the action of hydrobromic acid on glycidic acid. After removal of hydrobromic acid and extraction with ether, it is obtained in prismatic crystals, m. p. 89—90°. It is soluble in ether and water in all proportions. P. P. B.

**Amidolactic Acid.** By P. MELIKOFF (*Ber.*, 13, 1265—1266).—In support of the hypothesis that the formation of amidolactic acid by the action of ammonia on ethyl chlorolactate takes place in two stages, viz., that glycidic acid is first produced by the elimination of hydrochloric acid, and then converted into amidolactic acid by direct union with ammonia, the author states that the β-amidolactic acid obtained by the action of ammonia on glycidic acid at 120° is identical with the acid derived from ethyl α- or β-chlorolactate.

Serine from silk has the constitution of an α-amidolactic acid.

W. C. W.

**Diethylidenelactamic Acid.** By W. HEINTZ (*Annalen*, 202, 375—376).—A claim for priority.

**Action of Iodine on the Silver Salts of Bibasic Acids.** By K. BIRNBAUM and J. GAIER (*Ber.*, 13, 1270—1272).—On gently heating an intimate mixture of iodine and silver succinate, malate, fumarate, or tartrate, the following changes occur:—The silver and iodine combine, the acid splits up into anhydride and oxygen, and the nascent oxygen attacks the anhydride, converting a portion of it into carbonic oxide, carbonic anhydride, and water; the remainder of the anhydride unites with the water, forming an anhydro-acid. This reaction is in certain respects analogous to the electrolytic decomposition of aqueous solutions of these acids.

Silver oxalate is completely converted by the action of iodine into silver iodide and carbonic anhydride. W. C. W.

**Preparation of Malonic Acid.** By E. BOURGOIN (*Compt. rend.*, 90, 1289—1291).—100 grams of monochloroacetic acid are dissolved in their own weight of water and saturated with potassium carbonate, 71 grams of powdered potassium cyanide are then added, and the whole is carefully heated on a water-bath; a brisk ebullition, attended by considerable evolution of heat, ensues, but the liquid remains perfectly colourless. To this solution twice its volume of strong hydrochloric acid is added, the potassium chloride which separates is removed, and the whole is then saturated with hydrochloric acid gas; the potassium chloride and sal-ammoniac are again separated, washed with hydrochloric acid, and the liquid is evaporated nearly to dryness on a water-bath; the residue is exhausted with ether and the ethereal solution distilled, when about 70 grams of perfectly pure malonic acid are obtained. From the mother-liquors, by suitable treatment, about 20 grams more of the acid can be procured, which requires recrystallisation from ether to purify it. Although a small quantity of acetic acid is formed, according to the equation  $C_2H_3O_2 = CO_2 + C_2H_4O_2$ , the yield of malonic acid is almost theoretical. J. W.

**Synthesis of Citric Acid.** By E. GRIMAUX and P. ADAM (*Compt. rend.*, 90, 1252—1255).—The artificial formation of citric acid was realised in the following manner:—Symmetrical dichloroacetone was prepared by oxidation of the symmetrical dichlorhydrin of glycerol. It was purified by combination with sodium hydrogen sulphite and then heated in a water-bath with concentrated hydrocyanic acid. The cyanodichloroacetone, which is a crystalline body, was not isolated, but treated directly with hydrochloric acid; the product, when the reaction was complete, was distilled in a vacuum and the residue taken up by ether. On evaporation a thick syrup remained, which, after a few days, solidified to a mass of crystals of dichloroacetic acid,—



These crystals were in the form of transparent laminæ, fusible at 90—92°; very soluble in alcohol, water, and ether; not volatile without decomposition, except at a very gentle heat, when partial sublimation takes place.

The dichloroacetic acid was saturated with sodium carbonate and heated with two molecules of potassium cyanide in concentrated solution; the sodium dicyanoacetate was not separated but saturated with hydrochloric acid gas, and heated in a water-bath for 15 hours. After volatilising the hydrochloric acid, the citric acid was extracted from the residue by careful neutralisation and precipitation with milk of lime. The insoluble lime salt was decomposed by sulphuric acid, and the solution, after concentration in a vacuum, was left to spontaneous evaporation.

The identity of the artificial product with the natural acid was proved by analysis and by crystallographic comparison under the microscope. Its melting point was  $146-147^{\circ}$ . J. W.

**Electrolysis of Benzene.** By A. RENARD (*Compt. rend.*, **91**, 175—177).—The electrolysis of a mixture of benzene, alcohol, and dilute sulphuric acid gives a crystalline product soluble in water, alcohol, and ether. This substance the author names *isobenzoglycol*, and assigns to it the formula  $C_6H_5(OH)_2$ . Heated in a sealed tube with acetic acid it yields *isobenzoglycol diacetate*,  $C_6H_5(OAc)_2$ . It is insoluble in water, but soluble in alcohol or ether (m. p.  $121^{\circ}$ , b. p. about  $300^{\circ}$ ).

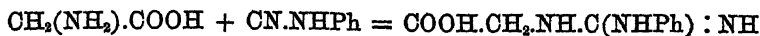
R. R.

**Influence of Constituents of Wood Spirit on the Production of Dimethylaniline.** By G. KRÄMER and M. GRODZKY (*Ber.*, **13**, 1005—1010).—The most hurtful constituent of crude wood-spirit is acetone; it lessens not only the yield of volatile bases, such as dimethylaniline, but also that of the non-volatile ammonium compound. Further, the violet obtained by the oxidation of such bases is not good. By using pure acetone alone, a base was obtained boiling at  $220-230^{\circ}$ , which on oxidation yielded a blackish-green mass. The base produced by this acid belongs to the acetonamine bases, and has the composition  $Me_2C:NPh$ . From this it is seen that 1 mol. acetone uses 1 mol. aniline. The presence of about 10 per cent. of water in pure methyl alcohol has very little influence on the yield of methylated aniline. Every increase of the proportion of methyl alcohol to aniline above the theoretical amount tends to decrease the yield of dimethylaniline, but increases that of the non-volatile ammonium compounds. Impure methyl alcohols yield smaller quantities of volatile bases, and the tubes on opening show much higher pressure, owing to the formation, in some cases, of methyl ether. A mixture of 4.8 c.c. of ethyl with 30 c.c. methyl alcohol gave the same yield as pure methyl alcohol. When the higher alcohols are used, they are partially decomposed into water and the corresponding olefines.

P. P. B.

**Aromatic Guanidine-compounds.** By F. BERGER (*Ber.*, **13**, 992—994).—*Glycolmonophenylguanidine*,  $C_6H_5N_3O_2$ , is obtained by the action of an alcoholic solution of glycocine containing a little ammonia on phenylcyanamide. The residue obtained on evaporating the solution to dryness, is dissolved in hydrochloric acid and ammonia added, when the above compound is precipitated in small, round, yellow grains. It turns brown at  $240^{\circ}$ , and melts at  $260^{\circ}$  with decomposition. By evaporation of its solution in hydrochloric acid, it is

decomposed, glycocine being formed. Its formation is expressed as follows:—



Attempts to prepare the isomeride phenylglycocycamine from phenylglycocine and cyanamide have proved unsuccessful.

The *hydrochloride* of  $\beta$ -dicyandiorthotolylguanidine,  $\text{C}_{23}\text{H}_{22}\text{N}_4\text{Cl} + \text{H}_2\text{O}$ , is obtained by boiling dicyandiorthotolylguanidine with aniline for half an hour; ammonia is then evolved, and when the product is poured into hydrochloric acid, the above compound separates out. It is sparingly soluble in hot alcohol, forming a dark red solution, from which it separates on cooling in fine needles of a brownish-red colour and violet lustre.

P. P. B.

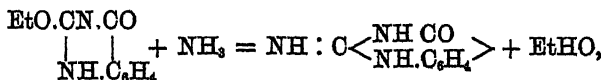
**Creatine-compounds of the Aromatic Group.** By P. GRIESS (*Ber.*, 13, 977—979).—1. *Orthobenzylglycocycamidine*,



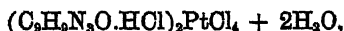
This compound is obtained in a manner analogous to glycocycamidine, viz., by the action of aqueous solutions of cyanamide on 1 : 2 amidobenzoic acid, thus:—



It is also formed when the compound  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$ , described by the author (*Ber.*, 2, 417) as resulting from the action of cyanogen on an alcoholic solution of 1 : 2 amidobenzoic acid, is treated with ammonia, thus:—



$\alpha$ -*Orthobenzylcreatinine*,  $\text{NH} : \text{C} \begin{array}{c} \text{NMe.CO} \\ \text{NH.C}_6\text{H}_4 \end{array} >$ , is obtained by acting on an alkaline solution of orthobenzylglycocycamidine with methyl alcohol and methyl iodide in the cold. It crystallises from water in small shining needles, sparingly soluble in hot water and ether, but easily in boiling alcohol. It has a bitter taste and neutral reaction; melts to a colourless oil and may be distilled; alkalis do not act on it. The *hydrochloride*,  $\text{C}_6\text{H}_7\text{N}_3\text{O.HCl.H}_2\text{O}$ , crystallises in narrow leaflets, easily soluble in cold water. The *platinochloride*,



crystallises from hot water in bright yellow needles, or in small rhombic six-sided prisms.

$\beta$ -*Orthobenzylcreatinine*,  $\text{C}_6\text{H}_9\text{N}_3\text{O}$ , is obtained in a manner similar to benzylglycocycamidine by acting on the compound  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$  with methylamine, in sealed tubes at  $100^\circ$ . It crystallises from water in white needles. In many properties it resembles the  $\alpha$ -derivative, but differs from it in being soluble in alkaline solutions, and reprecipitated from them by acetic acid. The *hydrochloride*,  $\text{C}_6\text{H}_9\text{N}_3\text{O.HCl}$ , forms small tables or prisms having vitreous lustre. It is decomposed by

pure water, and can only be crystallised from water containing hydrochloric acid.  $\alpha$ -Benzylcreatinine has stronger basic properties than the  $\beta$ -derivative. The  $\beta$ -platinochloride,  $(C_9H_8N_2O.HCl)_2PtCl_4$ , forms pale yellow narrow leaflets, united into stellate groups. It is only sparingly soluble in hot water. P. P. B.

**Aromatic Amidoketones.** By O. DOEBNER (*Ber.*, 13, 1011—1014).—*Benzoyl-phthalylanilide*,  $C_{21}H_{13}NO_3$ , is obtained by heating benzoic chloride with phthalylanilide and zinc chloride at  $180^\circ$ . The product, after recrystallisation from glacial acetic acid, yields this compound in large colourless needles (m. p.  $183^\circ$ ). It is neither acted on by acids nor by alkalis, is insoluble in water, and only sparingly soluble in alcohol or ether. When boiled with alcoholic potash, it yields phthalic acid and benzoylaniline.

*Benzoylaniline*,  $C_9H_7.CO.C_6H_4.NH_2$ , crystallises from dilute alcohol in colourless, shining leaflets (m. p.  $124^\circ$ ). It is but sparingly soluble in water, largely soluble in alcohol, ether, or glacial acetic acid. Hydrochloric acid dissolves it easily, forming a hydrochloride, from which alkalis and ammonia precipitate the base. Its hydrochloride crystallises from water in large crystals, the sulphate in needles which are less easily soluble than the hydrochloride. The platinochloride crystallises in yellow needles. P. P. B.

**An Azobenzenesulphonic Acid.** By MAHRENHOLTZ and GILBERT (*Annalen*, 202, 331—340).—This acid may be prepared from metanitrobenzenesulphonic acid by two methods. In the first process, sodium amalgam in theoretical quantity is added to a concentrated solution of potassium metanitrobenzenesulphonate. The action being ended, the solution is acidified with sulphuric acid, and the sodium sulphate removed by crystallisation, evaporation, and addition of alcohol. Finally, the mother-liquor is treated with barium carbonate, and the sparingly soluble barium azobenzenesulphonate collected.

A better process consists in adding to potassium metanitrobenzenesulphonate dissolved in six times its weight of cold water, half its volume of zinc-dust, and caustic potash in excess. The mixture is stirred and heated on the water-bath until hydrogen begins to escape, then rapidly filtered to avoid formation of hydrazo-acid, and the zinc precipitated by carbonic acid. Potassium azobenzenesulphonate may be separated from the filtrate by crystallisation.

*Azobenzenesulphonic acid*,  $C_6H_4(SO_3H)N:N.C_6H_4(SO_3H)$ , separated from its barium salt by sulphuric acid, remains on evaporation of its solution as a syrup, which crystallises on standing over sulphuric acid. It is deliquescent, and very soluble in alcohol and ether. It yields only neutral salts, of which those of ammonium, potassium, sodium, barium, and calcium are described: they are easily soluble in water, with the exception of the barium salt.

*Azobenzenesulphonic chloride*,  $C_{12}H_8N_2S_2O_4Cl_2$ , is easily formed by warming the dry potassium salt with phosphoric chloride, washing with water, drying, and exhausting with ether. It forms ruby-red needles (m. p.  $166^\circ$ ). The chloride dissolves easily in absolute alcohol, and on concentrating the solution and allowing it to stand, golden-

yellow needles of *ethyl azobenzenesulphonate*,  $C_{12}H_9EtN_2S_2O_6$ , separate, (m. p.  $100^\circ$ ). These are scarcely soluble in water, but soluble in alcohol and ether.

*Azobenzenesulphonamide*,  $C_{12}H_9N_2S_2O_4(NH_2)_2$ , is formed by treating the chloride with strong ammonia, evaporating, and extracting the residue with boiling alcohol, from which it separates in yellow needles (m. p.  $295^\circ$ ) or in crusts of radiating groups of prisms. It is sparingly soluble in boiling water and alcohol. A body similarly constituted, but having quite different properties, is obtained by warming a solution of metanitrobenzenesulphonamide in caustic soda with zinc-dust, and precipitating with hydrochloric acid. This body (m. p.  $254^\circ$ ) is very sparingly soluble in alcohol, ether, benzene, toluene, and acetic acid, and crystallises from hot alcohol in small reddish-yellow needles. Paranitrobenzenesulphonamide (m. p.  $131^\circ$ ) on similar treatment yields an azobenzenesulphonamide (m. p.  $176^\circ$ ), which is much more soluble in alcohol and water, and crystallises in yellow tables.

*Hydrazobenzenesulphonic acid*,  $C_{12}H_{12}N_2S_2O_6 \cdot 3H_2O$ , is obtained from the azo-compound by heating it with ferrous sulphate and caustic soda in excess, by the prolonged action of sodium amalgam, by prolonged boiling with zinc and caustic potash, but most easily by the action of stannous chloride. A solution of the azo-acid becomes very hot when mixed with stannous chloride, and after 48 hours the whole of the hydrazo-acid crystallises out in colourless monoclinic prisms, with many secondary faces. It is sparingly soluble in hot water, less so in cold, and insoluble in alcohol or ether. It is not converted into the amido-acid by digestion at a high temperature with stannous chloride or with hydriodic acid. Potassium, barium, and lead salts have been prepared.

An acid chloride could not be obtained by the action of phosphoric chloride either on the acid or on its potassium salt. The amide,



is apparently formed by heating the alcoholic solution of azobenzenesulphonamide (m. p.  $295^\circ$ ) with stannous chloride. It separates from the filtrate in white prisms.

Ch. B.

**Two Azobenzenedisulphonic Acids.** By H. v. REICHE (*Annalen*, 203, 64—72).—Two nitrobenzenedisulphonic acids were prepared from benzenemetadisulphonic acid, and were purified by the method described by Heinzelmann (*Annalen*, 188, 157—160, and this Journal, 1877, p. 771). In order to prepare the azo-derivatives, the barium salts of these acids are boiled with concentrated baryta-water and zinc-dust until a rapid evolution of hydrogen takes place, the mixture is then filtered, and the barium and zinc precipitated by carbonic acid. The filtrate deposits needle-shaped crystals of *barium azobenzenedisulphonate*.

*a-Azobenzenedisulphonic acid*,  $(SO_3H)_2C_6H_3 \cdot N \cdot N \cdot C_6H_3(SO_3H)_2$ , is a dark syrupy liquid, forming soluble salts. It crystallises when left in a vacuum over sulphuric acid, but speedily deliquesces on exposure to the air. It is precipitated by alcohol from an aqueous solution as a resinous mass. The *potassium salt*,  $C_{12}H_7K_2N_2S_4O_{12} + 3H_2O$ , forms



microscopic prisms soluble in water, but insoluble in alcohol; the *ammonium salt* is a yellow crystalline mass, soluble in alcohol. The *barium salt* is deposited in white needles containing  $5\text{H}_2\text{O}$ , insoluble in alcohol. The *lead salt* is precipitated from the aqueous solution by alcohol as a crystalline powder.

*α-Hydrazobenzenedisulphonic acid*—



prepared by the action of stannous chloride on azobenzenedisulphonic acid, is a syrupy liquid which bears the closest resemblance to the azo-acid. The *potassium salt*,  $\text{C}_{12}\text{H}_8\text{K}_2\text{N}_2\text{S}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ , forms small plates; the *acid potassium salt*,  $\text{C}_{12}\text{H}_{10}\text{K}_2\text{N}_2\text{S}_4\text{O}_{12} + 2\frac{1}{2}\text{H}_2\text{O}$ , crystallises in reddish scales of a silky lustre. The *barium salt*,  $\text{C}_{12}\text{H}_8\text{Ba}_2\text{N}_2\text{S}_4\text{O}_{12} + 7\frac{1}{2}\text{H}_2\text{O}$ , forms efflorescent needles insoluble in alcohol, and the *lead salt* crystallising with  $4\text{H}_2\text{O}$  is also efflorescent.

By the action of nitrous acid on the hydrazo-acid, benzenemetadisulphonic acid is produced.

The following salts of *β-azobenzenedisulphonic acid* were prepared:— $\text{C}_{12}\text{H}_8\text{K}_2\text{N}_2\text{S}_4\text{O}_{12}\cdot 3\text{H}_2\text{O}$  and  $\text{C}_{12}\text{H}_8\text{Pb}_2\text{N}_2\text{S}_4\text{O}_{12}\cdot x\text{H}_2\text{O}$  form red crystalline crusts insoluble in alcohol; the barium salt is deposited in yellowish-red flat needles containing 4 mols. of water of crystallisation.

*β-Azobenzenedisulphonic chloride*,  $\text{C}_{12}\text{H}_8\text{N}_2\text{S}_2\text{O}_6\text{Cl}_4$ , crystallises from ether in broad needles (m. p.  $58^\circ$ ). By the action of ammonia on the preceding compound the amide is obtained in white needle-shaped crystals (m. p.  $222^\circ$ ), which are sparingly soluble in warm alcohol.

*β-Hydrazobenzenedisulphonic acid* forms crystalline potassium and barium salts. If the solution of the acid is half neutralised with potash, and treated with nitrous acid, diazobenzenedisulphonic acid is produced.

W. C. W.

**Two Azotoluenesulphonic Acids.** By A. T. NEALE (*Annalen*, 203, 73—83).—The potassium salt of *azotoluenesulphonic acid*,  $(\text{SO}_3\text{H})\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Me}(\text{SO}_3\text{H}) + 7\frac{1}{2}\text{H}_2\text{O}[\text{Me}:\text{N}:\text{SO}_3\text{H}=1:2:4]$ , is obtained by boiling an aqueous solution of potassium orthonitrotolueneparasulphonate with potash and zinc-dust. When the hydrogen begins to escape in considerable quantities, the mixture is filtered, in order to prevent the further reduction of the compound to orthamidoparatoluenesulphonic acid. *Potassium azotoluenesulphonate*,  $\text{C}_{14}\text{H}_{11}\text{K}_2\text{N}_2\text{S}_2\text{O}_6 + 2\frac{1}{2}\text{H}_2\text{O}$ , forms beautiful red prisms, which dissolve freely in hot water, but require 100 parts of water at  $18^\circ$  to dissolve 2.56 parts of the anhydrous salt. From the potassium salt, the other metallic azotoluenesulphonates can be prepared by double decomposition. The *barium* and *lead salts* crystallise in red-coloured prisms, containing 4 mols.  $\text{H}_2\text{O}$ . They are sparingly soluble in water. The *calcium salt* forms freely soluble red crystals containing  $5\text{H}_2\text{O}$ . The free acid crystallises in long prisms of a pink colour, which decompose at  $180^\circ$  without melting. The *sulphonic chloride*,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{S}_2\text{O}_6\text{Cl}_2$ , is deposited from a solution in hot benzene in red-coloured prisms containing 2 mols. benzene, which escape on exposure to the air. The chloride (m. p.  $220^\circ$ ) is sparingly soluble in ether. *Hydrazotoluenesulphonic acid*,  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{S}_2\text{O}_6 + 2\frac{1}{2}\text{H}_2\text{O}$ , separates as a white, crystalline,

sparingly soluble powder, when an aqueous solution of the azo-acid is treated with stannous chloride. On exposure to the air, the acid assumes a red colour, due to its oxidation to the azo-acid. The hydrazotoluenesulphonates are freely soluble in water, the potassium salt,  $C_{14}H_{14}K_2N_2S_2O_6$ , is anhydrous; the barium salt crystallises with 5 and the calcium salt with  $3\frac{1}{2} H_2O$ . They are both efflorescent. The crystals of lead hydrazotoluenesulphonate contain  $2\frac{1}{2} H_2O$ , and resemble calcium oxalate in form.

2. *Azotoluenesulphonic acid* [Me :  $SO_3H$  : N = 1 : 2 : 4], prepared from potassium paranitrothotoluenesulphonate forms brown-coloured rhombohedrons containing  $7\frac{1}{2} H_2O$ . The crystals are freely soluble in water and alcohol; they melt in their water of crystallisation at  $100^\circ$ , and the anhydrous acid decomposes at  $190^\circ$  without melting. The following salts were prepared:  $C_{14}H_{13}K_2N_2S_2O_6 + 3H_2O$ ,  $C_{14}H_{13}CaN_2S_2O_6 + 3H_2O$ , yellow crystals;  $C_{14}H_{13}PbN_2S_2O_6 + 2H_2O$ , dark-brown crystals. These three salts are freely soluble in water; the barium salt forms orange-coloured microscopic needles (containing 1 mol.  $H_2O$ ), sparingly soluble in water. *Azotoluenesulphonic chloride* is deposited from benzene in deep red-coloured crystals (m. p.  $194^\circ$ ). The *amide* is a yellow crystalline compound (m. p.  $207^\circ$ ), soluble in alcohol. The hydrazo-acid has not yet been obtained. An attempt to prepare it by the action of stannous chloride on the azo-acid yielded paramidotolueneorthosulphonic acid.

W. C. W.

**An Azoxybenzenesulphonic Acid.** By C. BRUNNEMANN (*Annalen*, 202, 340—350).—Of the three known nitrobenzenesulphonic acids only the meta-compound has been reduced to azoxy-acid. This may be effected, but not satisfactorily, by heating with alcoholic potash, or with zinc and potash. The best process consists in boiling the acid for four to six hours with alcoholic potash under an excess pressure of 400 mm. of mercury. The aqueous solution of the product, when saturated with carbonic anhydride and evaporated, deposits the potash salt, which may be obtained in needles by crystallisation.

*Azoxybenzenesulphonic acid*,  

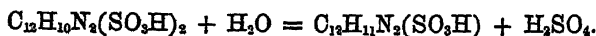
$$\begin{array}{c} C_6H_4(SO_3H).N \\ | \\ C_6H_4(SO_3H).N \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} O$$
, is obtained by de-

composing its barium salt with dilute sulphuric acid. It forms microscopic needles, which are very hygroscopic, and soluble in alcohol, ether, and water (m. p.  $125^\circ$ ). Only neutral salts could be obtained; those of ammonium, potassium, barium, calcium, and lead are described. The barium and lead salts are sparingly soluble in water, the others easily soluble.

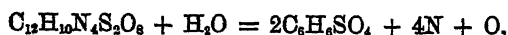
*Azoxybenzenesulphonic chloride*,  $C_{12}H_9N_2S_2O_6Cl_2$ , is easily produced by warming the potassium salt with phosphoric chloride. It is easily soluble in benzene and ether, and crystallises from toluene in yellowish-red oblique rhombic prisms (m. p.  $138^\circ$ ). On heating it with water at  $140^\circ$  not only azoxy-, but also much hydrazo-benzenesulphonic acid is formed. Treated with strong ammonia it yields an amide,  $C_{12}H_9N_2S_2O_6(NH_2)_2$ , crystallising in yellow monoclinic prisms (m. p.  $273^\circ$ ), very sparingly soluble in hot water, more easily in alcohol.

The free azoxy-acid is not acted on by dry bromine. Its solution is unaffected by sulphurous acid or by nitrous acid, but hydrogen sulphide passed into its ammoniacal solution reduces it to azo-acid. The same reduction is effected by sodium amalgam, whilst acid stannous chloride converts it into the hydrazo-acid.

The author confirms the statements of Mahrenholtz and Gilbert with regard to hydrazobenzenesulphonic acid, and describes several new salts of it. It cannot be reduced to amido-acid; and neither the inverse change, nor the oxidation of azo- to azoxy-acid, can be effected by potassium permanganate. Water has little action on it, even at 240°. Dilute hydrochloric acid at 230° partly decomposes it into sulphuric acid and benzidine. In this reaction, benzidinesulphonic acid is first formed, and may be detected by heating the hydrazo-acid with strong hydrochloric acid at 140° for five hours, evaporating and boiling the residue with barium carbonate, when brilliant tables of Griess's barium benzidinesulphonate may be obtained (*Annalen*, 154, 213). The reaction may be thus formulated—



When hydrazobenzenesulphonic acid is suspended in water, and treated with nitrous acid, it yields a diazo-compound,  $C_{12}H_{10}N_4S_2O_8 \cdot 2H_2O$ , fully described by Balentine. Boiling with water decomposes this compound, thus—



the liberated oxygen oxidising a portion of the substance.

The phenolsulphonic acid formed yields a barium salt,



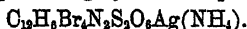
and a potassium salt,  $C_6H_4(OH).SO_3K \cdot 1\frac{1}{2}H_2O$ , the solutions of which give a violet colour with ferric chloride. Treated with chromic mixture, they evolve an odour of quinone: the acid is probably therefore a para-compound. Evaporation with strong nitric acid converts the free acid into *dinitrophenolsulphonic acid*, which yields both a neutral and an acid potassium salt.

Ch. B.

**Dibrom- and Tetrabrom-hydrazobenzenesulphonic Acids.** By O. JURDAN (*Annalen*, 202, 360—371).—Hydrazobenzenesulphonic acid is not acted on by dry bromine; but when the finely-powdered acid is covered with at most twice its weight of water, and bromine gradually added until a little acid remains undissolved, a mixture of tetrabrominated and dibrominated derivatives is obtained in solution. On concentrating the filtered liquid and allowing it to stand, the tetrabrominated acid separates, and may be purified by crystallisation from boiling water with the aid of animal charcoal. The process is repeated until the mother-liquor forms a brown syrup; from this the dibromo-acid may be extracted by evaporating to dryness, dissolving in water, precipitating with basic lead acetate, and decomposing the precipitate by hydrogen sulphide. By crystallisation from water with aid of animal charcoal it may be obtained pure.

*Tetrabromhydrazobenzenesulphonic acid,*

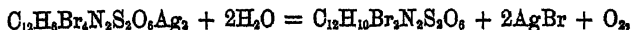
is obtained by very slow crystallisation in transparent, almost colourless, efflorescent tables. When rapidly deposited, the crystals are needles with only 2 mols. of water. The acid is easily soluble in water, less so in alcohol and ether. It is decomposed by sunlight and by heat. At  $170^\circ$ , the crystals become black and insoluble in the usual solvents, in acids, or in alkalis. It yields a brown solution with concentrated sulphuric acid, from which water separates brown flocks. It forms both neutral and acid crystalline salts, of which those with ammonium, potassium, barium, calcium, lead, and silver, have been prepared, and are fully described. The acid silver salt,  $\text{C}_{12}\text{H}_7\text{Br}_4\text{N}_2\text{S}_2\text{O}_6\text{Ag}$ , crystallises from water in oblique rhombic prisms; the neutral salt,  $\text{C}_{12}\text{H}_2\text{Br}_4\text{N}_2\text{S}_2\text{O}_6\text{Ag}_2$ , is obtained by double decomposition in microscopic tables, scarcely soluble in water. Hot dilute nitric acid converts it almost completely into the acid salt. Its ammoniacal solution yields on evaporation grey-coloured prisms,



On warming the potassium salt with phosphoric chloride, a dirty yellow mass is obtained, which dissolves in ether, but does not crystallise from it. It is probably an acid chloride; it melts with decomposition above  $210^\circ$ .

On passing nitrous acid into a solution of the tetrabrominated acid, yellow tabular crystals of a diazo-compound,  $\text{C}_{12}\text{H}_5\text{Br}_4\text{N}_2\text{S}_2\text{O}_6$ , separate. They are sparingly soluble in water or alcohol. The decomposition-products with water and hydrobromic acid could not be obtained pure.

The tetrabrominated acid does not part with its bromine when treated with sodium amalgam. Its silver salt is decomposed by water at  $200-210^\circ$ , thus—



part of the substance being oxidised by the liberated oxygen.

*Dibromhydrazobenzenesulphonic acid*,  $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{N}_2\text{S}_2\text{O}_6\cdot\text{H}_2\text{O}$ , crystallises in delicate colourless needles, which easily form a reddish solution in water, but are only sparingly soluble in alcohol or ether. It forms neutral and acid salts, of which those with potassium, barium, calcium, lead, and silver are described. The silver salt,



forms dirty white prisms, easily soluble in water, and blackened by light.

An acid chloride could not be obtained. The diazo-compound, obtained in the usual way, forms yellow rhombic prisms, which deflagrate at  $90^\circ$ .

The silver salt above mentioned is decomposed by water at  $220^\circ$ , yielding metallic silver, some silver bromide, and free acid.

Ch. B.

**Diazo-compound of Hydrazobenzenesulphonic Acid.** By W. BALENTINE (*Annalen*, 202, 351—360).—This diazo-compound,  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{S}_2\text{O}_6 + 2\text{H}_2\text{O}$ , is prepared, either by passing nitrous acid into

water, holding in suspension the finely powdered acid, and precipitating with alcohol, or better, by passing the gas into a cold solution of the potassium salt of the acid. It is deposited from its warm aqueous solution in rhombic tables, or may be precipitated therefrom by alcohol in the form of slender needles of a dirty white colour. It is tolerably soluble in warm water, but with difficulty in cold water or alcohol. It explodes at 93—94°, but slowly gives off nitrogen above 90°, leaving a brown amorphous residue,  $C_{12}H_{10}S_2O_8$ , which is not taken up by the usual solvents, but dissolves in alkaline solutions, without, however, forming crystallisable compounds. When heated with absolute alcohol under an excess pressure of 400 mm. of mercury no aldehyde is produced, and the amorphous brown product of the action is quite insoluble in alcohol, water, ether, or aniline, but soluble in alkalis, forming sparingly soluble uncrystallisable compounds. Analysis yielded very discordant results.

If the solution obtained by passing nitrous acid into potassium hydrazobenzenesulphonate until gas begins to be evolved is evaporated to dryness, the residue yields by crystallisation *acid potassium dinitrophenolsulphonate*, from which the free acid may be extracted by treating it with sulphuric acid, and digesting with alcohol and ether. Dinitrophenolsulphonic acid,  $C_6H_4(NO_2)_2(OH).SO_3H.3H_2O$ , forms greenish oblique rhombic prisms, which dissolve easily in water, less easily in alcohol and ether. It decomposes at 160°, and forms both acid and neutral salts. The acid potassium salt is yellow, the neutral red; both are readily soluble in water and weak alcohol. Ch. B.

**Action of Sulphuric Acid on Aromatic Sulphydrates.** By R. OTTO (*Ber.*, 13, 1290—1292).—The author confirms the accuracy of Stenhouse's observation (*Annalen*, 149, 247), that thiophenol is converted into phenyl disulphide by the action of sulphuric acid. A yellowish-white compound insoluble in alcohol and ether is formed at the same time.

Paratoluene and benzyl sulphydrates undergo analogous changes when treated with sulphuric acid or sulphuric monochloride.

W. C. W.

**Beckurts' Toluenemetasulphonic Acid.** By R. OTTO (*Ber.*, 13, 1292—1294).—A chemical examination of a specimen of Beckurts' toluenemetasulphonic acid (*Ber.*, 10, 943; and this Journal, 1877, 2, 774) shows that this substance is a mixture of toluenepara- and ortho-sulphonic acids. This result agrees with Fahlberg's statement (*Ber.*, 12, 1048; and this Journal, 1879, Abst., 804). W. C. W.

**Constitution of the Sulphinic Acids.** By R. OTTO (*Ber.*, 13, 1272—1283).—*New Syntheses of Sulphones.*—The sulphones can be readily prepared by warming an alcoholic solution of a sodium sulphinite with an alcoholic bromide. When the reaction is complete, the alcohol is distilled off and the residue poured into water.

*Ethylphenylsulphone*,  $PhEtSO_2$ , prepared by this process, crystallises in monoclinic plates (m. p. 42°), and is identical with the sulphone which Beckmann obtained (*J. pr. Chem.*, 17, 458) by the oxidation of ethyl-phenyl sulphide with potassium permanganate. It is easily pre-

pared by adding potassium permanganate to a solution of ethyl-phenyl sulphide in warm glacial acetic acid.

*Ethylparatolylsulphone*,  $\text{Et}(\text{C}_6\text{H}_4\text{Me})\text{SO}_2$ , crystallises in rhombic plates (m. p.  $56^\circ$ ) insoluble in cold water, but freely soluble in ether, benzene, chloroform, and warm alcohol. This substance is also formed by the oxidation of ethyl paratolyl sulphide, a colourless liquid (b. p.  $220^\circ$ , sp. gr. 1.0016 at  $17.5^\circ$ ) insoluble in water, but miscible in all proportions with alcohol, ether, benzene, and glacial acetic acid. *Dibenzylsulphone*,  $(\text{CH}_2\text{Ph})_2\text{SO}_2$ , forms small colourless needles or prisms (m. p.  $150^\circ$ ) of a silky lustre. It is soluble in benzene, glacial acetic acid, and hot alcohol, and is converted by oxidation into benzoic and sulphuric acids.

*Paratolylbenzylsulphone*,  $\text{CH}_2\text{Ph}.\text{SO}_2.\text{C}_6\text{H}_4\text{Me}$ , crystallises in silky white needles (m. p.  $145^\circ$ ) soluble in alcohol, benzene, and glacial acetic acid. *Diethylsulphone*,  $\text{Et}_2\text{SO}_2$ , has been previously described. The author confirms Beckmann's statement (*loc. cit.*) that this compound is not attacked by nascent hydrogen. This observation is in direct opposition to v. Oefele's (*Ann.*, 132, 90). *Ethylenediphenylsulphone*,  $\text{Ph}.\text{SO}_2.\text{CH}_2.\text{CH}_2.\text{SO}_2.\text{Ph}$ , forms silky needles or plates (m. p.  $179.5^\circ$ ) sparingly soluble in hot water, more soluble in hot alcohol, benzene, and acetic acid. It also dissolves in a dilute solution of potash, forming potassium benzenesulphinate. At  $150^\circ$  ethylidene chloride acts on sodium paratoluenesulphinate, forming a compound which crystallises from alcohol in needles (m. p.  $200^\circ$ ).

The conversion of the sulphinic acids into sulphones favours the hypothesis that these acids are hydrides and do not contain the hydroxyl group, and also that the sulphur-atom acts as a hexad and

not as a tetrad, e.g., benzenesulphinic acid,  $\text{S}^{\text{VI}} \begin{cases} \text{C}_6\text{H}_5' \\ \text{O}'' \\ \text{O}'' \\ \text{H}' \end{cases}$ .

W. C. W.

**Benzyl Derivatives Containing Sulphur.** By R. OTTO and R. LÜDERS (*Ber.*, 13, 1283 — 1289). — Benzyl-hydrogen sulphide,  $\text{C}_6\text{H}_5.\text{CH}_2.\text{SH}$ , is not converted into the disulphide by the action of bromine, but yields an oily liquid, which is transformed into benzyl hydrogen sulphide by nascent hydrogen. *Dibenzylsulphone*—



can be prepared by oxidising with potassium permanganate a hot acetic acid solution of benzyl oxysulphide (m. p.  $133^\circ$ ) obtained by treating benzyl sulphide with cold nitric acid, sp. gr. 1.3. It is identical with the dibenzylsulphone resulting from the action of benzoic chloride on sodium benzylsulphinate.

*Benzyl thiobenzoate*,  $\text{Ph}.\text{COS}.\text{CH}_2\text{Ph}$ , formed by heating benzyl hydrogen sulphide and benzoic chloride at  $120^\circ$ , is deposited from an alcoholic solution in colourless triclinic crystals, which dissolve freely in hot acetic acid, benzene and ether.

This compound is decomposed by alcoholic potash into benzoic acid and benzyl-hydrogen sulphide, and is oxidised by potassium permanganate, forming benzoic and benzenesulphonic acids.

**Benzylsulphonic chloride**,  $C_7H_7.SO_2Cl$ , prepared by the action of phosphorus pentachloride on potassium benzylsulphonate, crystallises in yellowish-white silky needles or prisms (m. p.  $93^\circ$ ) soluble in warm benzene or ether. It is decomposed by hot water, yielding hydrochloric and benzylsulphonic acids. The sulphonamide,  $C_7H_7.SO_2.NH_2$ , forms white silky needles (m. p.  $102^\circ$ ).

The sulphonic chloride is converted into benzylsulphonic acid by warming with zinc-dust and water, or by reducing the solution in benzene to which a few drops of water have been added with sodium amalgam. The sodium salt of the acid crystallises in silky plates. The free acid is very unstable, and decomposes with evolution of sulphurous anhydride.

When potassium benzylsulphonate is fused with potash in a retort, toluene and a small quantity of benzene distil over, together with a white crystalline compound (m. p.  $106-110^\circ$ ), which is soluble in alcohol.

W. C. W.

**Synthesis of Ethereal Salts of Thiosulphonates.** By R. OTTO (*Ber.*, 13, 1282—1283).—*Ethyl thiobenzenesulphonate* or *ethyl phenyldisulphoxide*,  $PhSO_2.SEt$ , is formed on warming an alcoholic solution of ethyl bromide and potassium thiobenzenesulphonate (prepared by Spring's method, *Ber.*, 7, 1157), viz., by the action of potassium sulphide on benzenesulphonic chloride. Ethyl thiobenzenesulphonate is not attacked by water at  $120^\circ$ , but is easily saponified by potash, and decomposed by reducing agents.

W. C. W.

**Constitution of Tetranitrodiphenylcarbamide.** By S. M. LOSANITCH (*Ber.*, 13, 1297).—The dinitraniline (*Ber.*, 11, 1539, this Journal, 1879, Abst., 67) which is formed by the action of water on tetranitrodiphenyl-potassium carbamide obtained by treating tetranitrodiphenylcarbamide with alcoholic potash, can be easily converted into  $\alpha$ -dinitrophenol, which Salkowski (*Ber.*, 7, 373) has shown to have the constitution  $C_6H_4(OH)(NO_2)(NO_2) = [1 : 2 : 4]$ .

Tetranitrodiphenylcarbamide must have a similar constitution.

W. C. W.

**Diphenic Anhydride.** By C. GRAEBE and C. MENSCHING (*Ber.*, 13, 1302—1305).—Diphenic anhydride is formed together with diphenylene ketone by the action of one or two molecules of phosphorus pentachloride on 1 mol. of diphenic acid. It is also formed together with other products of decomposition by the distillation of diphenic acid. The anhydride is, however, best prepared by dissolving the acid in strong sulphuric acid at  $120^\circ$ , and pouring the liquid into water. Long-continued boiling in water has no effect on the anhydride. It decomposes at the temperature of boiling sulphur, splitting up into diphenylene ketone and carbonic anhydride. A *phthaléin* is formed when the anhydride is heated with phenol and stannic chloride. It is a red crystalline compound, dissolving in alkalis with a red coloration. Diphenic anhydride also forms a compound with resorcinol. A chloride, having the composition  $C_{28}H_{16}Cl_2O_5$  (m. p.  $128^\circ$ ), is obtained by gently warming a mixture of diphenic anhydride and phosphorus pentachloride.

W. C. W.

**Diamidotriphenylmethane.** By C. BÖTTINGER (*Ber.*, 13, 958—959).—This is a personal explanation, replying to the remarks of O. Fischer (*Ber.*, 13, 665) upon the base,  $C_{18}H_{18}N_2$  (diamidotriphenylmethane). The author contends for the correctness of the melting point as given by him (*Ber.*, 12, 975). P. F. B.

**Substitution of Phenyl.** By V. MERZ and W. WEITH (*Ber.*, 13, 1298—1302).—Diphenylamine is formed by heating aniline zinc chloride with phenol at  $250^\circ$ ,  $NH_2Ph + Ph.OH = NHPh_2 + H_2O$ .

By the action of ammonium-zinc chloride (1 part) on phenol (2 parts) at  $280^\circ$  for eight hours, a mixture of aniline, diphenylamine, and diphenyl ether is obtained.

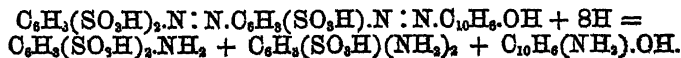
*Phenyl  $\beta$ -naphthylamine* is prepared by heating aniline and  $\beta$ -naphthol in molecular proportions with an excess of zinc chloride at  $180^\circ$  for six hours. The crude product is extracted with hydrochloric acid and with a hot solution of soda, and the residue is dried and distilled in a vacuum. The pure amine crystallises in colourless needles (m. p.  $108^\circ$ ) which dissolve freely in the usual solvents at their boiling points. When  $\beta$ -naphthol is heated at  $200^\circ$  with twice its weight of ammonium zinc chloride,  $\beta$ -naphthylamine and  $\beta$ -dinaphthylamine are formed. The product is extracted with hydrochloric acid to remove the  $\beta$ -naphthylamine, and boiled with a solution of soda. On dissolving the residue in hot benzene,  $\beta$ -dinaphthylamine is obtained in silver-white plates (m. p.  $170.5^\circ$ ), soluble in hot acetic acid. W. C. W.

**Conversion of  $\alpha$ -Naphthylamine into  $\alpha$ -Naphthyl Methyl Ether.** By A. HANTZSCH (*Ber.*, 13, 1347—1348).—A good yield of  $\alpha$ -naphthyl methyl ether,  $C_{10}H_7.OMe$ , is obtained by the action of zinc chloride on a mixture of methyl alcohol and naphthylamine at  $200^\circ$ . The crude product is treated with hydrochloric acid and extracted with a mixture of ether and benzene. On distilling the extract, naphthyl-methyl ether passes over at  $264^\circ$  as a colourless oily liquid miscible with alcohol, ether, and benzene. With picric acid it forms a red crystalline compound.

The corresponding ethyl ether can only be obtained in small quantities by this process.

*Dimethylnaphthylamine* can be easily prepared by heating naphthylamine hydrochloride with methyl alcohol at  $180^\circ$ . W. C. W.

**Biebrich Scarlet.** By W. v. MILLER (*Ber.*, 13, 980—982).—The author defends the view that this colouring matter contains the trisulphonic acid of an azo-compound,  $Ph.N:N.C_6H_4.N:NC_{10}H_6.OH$ , against the assertion of Nietzki (*Ber.*, 13, 800), who contends that it contains the mono- and di-sulphonic acids only. The author supports his position by the analysis of the sulphonic acids obtained by reducing the scarlet, from which mixture amidobenzenedisulphonic acid has been obtained, the formation of which can alone be explained by the existence of a trisulphonic acid, thus:—





The formation of a trisulphonic acid would depend on the conditions of temperature in preparing the "acid-yellow" from amidazobenzene, and it is easy to suppose that the temperature would rise sufficiently to produce it. Further, by treating "acid-yellow" with  $\beta$ -naphthol, the author has obtained a colouring matter having all the properties of Biebrich scarlet. P. P. B.

**Constitution of Phenanthrene.** By G. SCHULTZ (*Annalen*, **203**, 95—118).—In previous communications (*Annalen*, **196**, 1; *Ber.*, **11**, 215; **12**, 235; and this Journal, Abst., 1878, 511; 1879, 538 and 653), the author has shown, by a comparison of the crystalline form (monoclinic tabular crystals) and melting point ( $73.5^\circ$ ) of the methyl salts of diphenic acid from phenanthrene and from metanitrobenzoic acid, that these two diphenic acids are identical. He has also pointed out that the base melting at  $157^\circ$ , which Struve obtained together with benzidine by distilling diamidodiphenic acid with lime or baryta (*Ber.*, **10**, 75; this Journal, 1877, ii, 902) is *diamidofluorene*, and not a diamidodiphenyl.

*Diamidofluorene* is deposited from an alcoholic solution in grey needles, soluble in hot water and in hydrochloric acid. With dilute sulphuric acid, it yields a sparingly soluble salt. The crystals change colour on exposure to the air, and are easily attacked by oxidising agents.

*Diacetamidofluorene*,  $C_{13}H_9(NHAc)_2$ , crystallises in white glistening plates, which begin to decompose at  $250^\circ$ .

*Mononitrodiphenylene ketone*,  $\begin{matrix} C_6H_5-NO_2 \\ | \\ C_6H_4 \end{matrix} > CO$ , prepared by dissolving

diphenylene ketone in cold fuming nitric acid, is insoluble in water, but dissolves in hot alcohol, benzene, xylene, glacial acetic acid, or amyl alcohol. It forms needle-shaped crystals or plates (m. p.  $220^\circ$ ), which sublime readily. By the action of warm nitric acid, it is converted into the dinitro-derivative (m. p.  $290^\circ$ ), which on reduction with tin and hydrochloric acid yields a new base (m. p.  $286^\circ$ ), freely soluble in ethyl and amyl alcohols and in ethyl acetate.

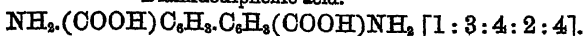
$\beta$ -*Dinitrodiphenic acid* is formed, together with the  $\alpha$ -modification, when nitric acid acts on diphenic acid. The isomeric acids are separated by means of the greater solubility of the barium salt of the  $\beta$ -acid. It can also be prepared by heating phenanthraquinone with a mixture of strong sulphuric and nitric acids, and pouring the crude product into water, when dinitrophenanthraquinone is precipitated. The mother-liquor deposits  $\beta$ -dinitrodiphenic acid when left at rest. The precipitate of dinitrophenanthraquinone is extracted with boiling acetic acid, which leaves the ordinary modification undissolved. On oxidising the acetic acid solution with chromic acid, a mixture of  $\alpha$ - and  $\beta$ -dinitrodiphenic acids is obtained, which is separated by conversion into the barium salts and fractional crystallisation.

$\beta$ -*Dinitrodiphenic acid* forms needle-shaped crystals (m. p.  $297^\circ$ ), insoluble in cold water, but soluble in alcohol. Its salts are freely soluble in water. *Barium  $\beta$ -dinitrophenate* crystallises with 4 mols.  $H_2O$  in large transparent triclinic prisms. The *methyl salt* crystallises

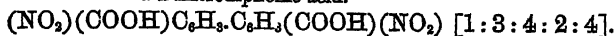
in pale yellow monoclinic plates (m. p. 131°), whilst *methyl α-dinitrophenate* forms small yellow monoclinic prisms (m. p. 177°).

The author represents the constitution of diamidodiphenic acid and the diphenyl-derivatives by the following formulæ:—

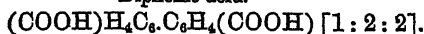
Diamidodiphenic acid.



α-Dinitrodiphenic acid.



Diphenic acid.



W. C. W.

**A Bromo-derivative of Nicotine.** By A. CAHOURS and A. ETARD (*Compt. rend.*, 90, 1315—1317).—One part of nicotine is dissolved in 50 parts of water, and 2 mols. of bromine added for every mol. of nicotine. A yellow flocculent resinous-looking precipitate falls, which, together with the mother-liquor, is heated gently to 65–70°, more bromine being added if required. The whole is then filtered and allowed to cool, when an abundant crystallisation of the bromo-derivative takes place. The undissolved portion treated separately with water at 70° yields a crystalline deposit similar to the preceding.

The crystals are in the form of red needles often more than 1 mm. in length, and are similar in colour to potassium dichromate. They are unalterable in the air, but are decomposed by water at a temperature higher than 70°. When dissolved in concentrated hydrobromic acid, they assimilate a molecule of HBr, forming the hydrobromide of the original derivative.

Analysis showed that the formula of the bromo-derivative is  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Br}_4$ . Huber's pentabromide is therefore probably the hydrobromide above mentioned, but the formula given to it by Huber contains 3 atoms less of hydrogen.

The tetrabromo-nicotine is decomposed and destroyed by an aqueous solution of potash.

J. W.

**Homatropine.** By A. LADENBURG (*Ber.*, 13, 1340).—On recrystallisation from absolute ether, homatropine is deposited in colourless transparent prisms, which melt between 95·5° and 98·5°. The crystals are hygroscopic, although they do not dissolve freely in water.

W. C. W.

**Non-identity of the Soluble Albuminoids of Crystallin with those of White of Egg and Serum.** By A. BÉCHAMP (*Compt. rend.*, 90, 1255—1258).—Many experimenters have examined this subject, but the results of their work do not appear to agree either among themselves or with those of the author. On the part of the latter, long and careful experiments have led him to conclude—(1) that the soluble portion of crystallin contains two distinct albumins clearly separable the one from the other, thus confirming the original observation of Frémy. (2) The substantial unity of the albuminoid substances must be denied, and their specific plurality affirmed.

3 l z

The coagulating power of these bodies was regarded as a property of only secondary importance; their purity was determined by immediate analysis and by their constant rotatory power, the latter property especially being adopted as the best criterion of the purity of these uncrystallisable substances. The following matters were isolated and characterised.

*Soluble Phacozymase*.—This substance remains dissolved in water after the solution has been precipitated by alcohol. Its aqueous solution begins to coagulate about 55°, and becomes violet when boiled for a few seconds with strong hydrochloric acid. It liquefies starch-paste, converting it into dextrin and possibly into dextrose. Its rotatory power for ( $\alpha$ ), = 41° to the left.

*Crystalbumin* is precipitable from its solution by alcohol. Its lævorotatory power in acetic solution for ( $\alpha$ ), = 80·3°, in ammoniacal solution = 76·6°. Like phacozymase, it turns violet when boiled in strong hydrochloric acid, but, unlike egg and serum albumin, its combination with basic lead acetate is not decomposed by carbonic anhydride.

The crude solution from crystallin has a rotatory power of 47·1°, which is very nearly the mean of the numbers already given. The insoluble portion of crystallin is in acetic solution lævorotatory to the extent 76·3°. It is, however, a mixture, for when dissolved in dilute hydrochloric acid it yields a precipitate on addition of ammonia, and this when redissolved in acetic acid has a rotatory power of 80·2°, the same as that of crystalbumin. This *crystalfibrin* is only slightly and with difficulty coloured violet by boiling in strong hydrochloric acid.

None of the above-mentioned rotatory powers are exactly identical with those of the albumins obtained from white of egg, from blood-serum, or from casein.

J. W.

**Lecithin and Nuclein in Yeast.** By O. LOEW (*Pflug. Archiv. Phys.*, 22, 62—68).—This paper is chiefly a criticism of Hoppe-Seyler's work on the subject, the author being of opinion that his (Hoppe-Seyler's) method of preparation, estimation, &c., was unsatisfactory. Great stress is laid on the readiness with which these bodies are decomposed by acids and alkalis, and an experiment is detailed showing that traces only of lecithin can be obtained from feebly acid yeast. The variable proportion of phosphorus (2—9 per cent.) found in nuclein from various sources, is, the author thinks, reason enough to doubt their identity.

W. N.

**Carbonyl-hæmoglobin.** By T. WEYL and B. v. ANREP (*Ber.*, 13, 1294—1296).—The compound of hæmoglobin with oxygen is rapidly converted into methæmoglobin by potassium permanganate and other oxidising agents, whilst the compound with carbonic oxide is only slowly attacked. On the addition of a few drops of ammonium sulphide to a solution of methæmoglobin, reduction takes place, and the absorption-bands characteristic of this body disappear. On passing oxygen through the liquid, the oxygen-compound of hæmoglobin is formed if the blood originally contained oxygen, but if it contained

carbonic oxide, then carbonyl-hæmoglobin is produced. This shows that oxygen-methæmoglobin is totally distinct from carbonyl-methæmoglobin, although they both exhibit the same spectrum.

*Detection of Carbonic Oxide in Blood.*—The blood must be preserved in a cold dark room, out of contact with air. Carbonic oxide is absent when ammonium sulphide or ferrous ammonium tartrate does not cause a reduction to hæmoglobin. It is present when the addition of a few drops of dilute (0.025 per cent.) solution of potassium permanganate leaves the blood red and clear, and does not produce methæmoglobin in 20 minutes. A similar quantity of the oxidising solution, added to fresh blood shaken with air, should change the colour to yellow, and produce a turbidity.

One per cent. solution of catechol or quinol at 40° may be used instead of potassium permanganate. W. C. W.

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## Physiological Chemistry.

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**Influence of Glycerol on the Decomposition of Proteids in the Animal Body.** By N. TSCHIRWINSKY (*Zeits. f. Biologie*, 15, 252—260).—This paper is a sequel to the preceding, the chief difference in the experiments being that this observer allowed the dog no fat, in order that the effect of the glycerol on the proteid metamorphosis might be the more evident, and used very much larger quantities.

The general result was an increase in the quantity of urine, and a slight fall in the elimination of urea.

The effect of large doses of glycerol appears to be sometimes hæmoglobinuria, and the urine frequently contains a substance which reduces copper solution (Ustimowitsch Plósz), and which is not sugar. Catillon finds that glycerol passes unchanged into the urine, when 4—6 grams are given for every kilogram of body weight. He estimates it in the urine by evaporating at 100°, extracting with alcohol, and evaporating the alcoholic solution to a syrupy consistence; in normal urine, the relation of the weight of this residue to the urea is 1.5 : 1.

The author then describes a method of estimating glycerol, based on the fact that it dissolves copper oxide in presence of excess of alkali, and calculates that in his experiments glycerol in quantities varying from 37 per cent. to 60 per cent. of the quantity given were eliminated unchanged with the urine. W. N.

**Influence of Glycerol on Proteid Tissue Change.** By L. LEWIN (*Zeits. f. Biologie*, 15, 243—251).—After some preliminary remarks on the chemical relations of glycerol, the author quotes Lauder Lindsay, Benavente, Davasse, and others, as to the fattening properties of glycerol. Catillon's experiments are discussed in some detail as the first real attempt to settle the question as to whether glycerol is a food or not.

Catillon found that guinea-pigs which maintained their weight on a certain diet gained one-fifteenth to one-tenth when 1 gram of glycerol was added. The same observer found that glycerol diminished the amount of urea excreted in man: hence he came to the conclusion that glycerol was a food in Voit's sense, "that it diminished the consumption of albuminoids." The author admits that the increase of weight after glycerol is well nigh proven, but remarks that excess of water will produce the same effect, and further that Catillon's experiments were on his own showing of doubtful value, since the diet was not regulated.

Immanuel Munk experimented on a dog in nitrogenous equilibrium, and found that doses up to 25 grams and 30 grams produced no appreciable effect on the proteid metamorphosis, whilst a dose of 40 grams caused diarrhoea.

The author made experiments on a dog, and the results are tabulated. The first table shows that nitrogenous equilibrium was maintained on a diet of 750 grams meat and 150 grams fat. The second table shows the effect of glycerol, *i.e.*, a slight increase in the urea eliminated, the average daily excretion being in the first case 51.84 grams, and in the second, 53.35 grams; the reverse was the case in Catillon's experiments.

The glycerol increases the amount of urine, and after discussing the possibility that the effects produced may be due to this diuresis, the author comes to the conclusion that glycerol exerts no influence on the total of proteid metamorphosis, as fats and carbohydrates have been shown to do, and which he illustrates by experiments on the same dog in a somewhat striking manner.

Doses of 300 grams of glycerol were found to be poisonous, producing tonic and clonic spasms, and incontinence of urine and faeces.

Davasse, *Das Glycerin*, übers. von Zeisse, Wien, 1860, 15; Ebstein u. Müller, *Berl., Klin. Wochenschr.*, 1875, Nr. 5; Schleich, *Wurtemb. Correspondenzblatt*, 44, 1874, Nr. 34; Catillon, *Étude des Propriétés Physiologiques et Thérapeutiques de la Glycerin*; *Arch. d. Physiol. Normale et Patholog.*, 1877, Nos. 1, 2; Munk, *Verhandl. der Physiol. Ges.*, zu Berlin, 13th Dec., 1878; Ustimowitsch, *Pflüger's Archiv*, Bd. 18, 458; Schultzen, *Berlin, Klin. Wochenschr.*, 1872, Nr. 35; Harnack, *Archiv. f. Klin. Med.*, 13, 6. W. N.

**Influence of the Supply of Water, the Secretion of Sweat, and Muscular Labour on the Elimination of Nitrogenised Decomposition Products.** By H. OPPENHEIM (*Pflüger's Archiv. Physiol.*, 22, 40—41).—During a 35 days' experiment, in which he was in a state of nitrogenous equilibrium, the author investigated the effect of varying physical conditions on the elimination of urea, with the following general results:—

(1.) Increased ingestion of water continued for some time produces at first an increase in the elimination, which gradually diminishes, until the quantity falls below normal, so that the average over the period is very little affected.

(2.) Injection of pilocarpine produced no especial effect either on the

nitrogen of the urine or fæces, even when water was taken to make up for the loss sustained by the increased secretion of sweat and saliva.

(3.) Muscular labour appears to increase the nitrogen eliminated only when carried to the extent of producing dyspnoea, and this is due not to increased muscular activity but to the new conditions which are set up.

W. N.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of Air on Fermentation.** By E. C. HANSEN (*Bied. Centr.*, 1880, 479—480).—By passing air through a fermenting mash, the number of yeast cells is increased twice or three times as much as if no air were bubbled through, and about twice the quantity of liquid is fermented, thus showing that a constant supply of oxygen is very favourable to fermentation.

J. K. C.

**Schizomycetic Fermentations. Part VI.** By A. FITZ (*Ber.*, 13, 1309—1312).—On fermentation, calcium lactate yields a trace of alcohol, propionic acid, and a small quantity of succinic acid. In a second experiment with a different kind of ferment, propionic and normal valeric acids were formed, together with calcium carbonate and a small quantity of ethyl alcohol. When Pasteur's butyric acid ferment is used, the chief product is butyric acid; small quantities of ethyl and butyl alcohol are also produced.

In the preparation of butyl alcohol from glycerol, the relative quantities of ethyl and butyl alcohols vary with the nature of the ferment. A small quantity of propyl alcohol is also obtained. In the fermentation of calcium glycerate by means of a species of *bacillus*, the chief product is formic acid, but a small quantity of methyl alcohol and acetic acid is also produced.

W. C. W.

**Influence of Fermentation on the Nitrogenous Constituents of Potato Mash.** By P. BEHREND and A. MORGEN (*Bied. Centr.*, 1880, 486—487).—During fermentation, the soluble acid amides become converted into amido-acids with loss of ammonia, which goes to the nourishment of the yeast; it appears also that more albumin is present in the fermented mash than in the unfermented, and this seems to point to the conclusion that during the fermenting process albumin has been built up from the amido-compounds through the agency of the yeast.

J. K. C.

**Influence of Boric Acid on Acetous Fermentation.** By A. HERZEN (*Bied. Centr.*, 1880, 487—488).—Boric acid appears to have no influence on the conversion of sugar into alcohol, but if added to a wine undergoing acetous fermentation, it entirely prevents further decomposition. The circumstance that boric acid is not a poison for most microscopic plants and for *Mycoderma cerevisiae*, favours the assumption that the decomposition of alcohol into acetic acid is a

purely chemical process, which is in some way prevented by the presence of boric acid. In order to test the truth of this assumption, into a flask A was poured 100 c.c. of distilled water, 10 per cent. pure alcohol, and a drop from the surface of a fermenting wine, full of *Mycoderma aceti*. Flask B contained 100 c.c. distilled water, 5 per cent. pure acetic acid, and a drop of the same wine. Flask C received 100 c.c. distilled water, 5 per cent. pure acetic acid, 5 per cent. saturated boric acid solution, and a drop of the decomposing wine. All three were closed with cotton wool, and placed in a bath at 25° C. The result was that after eight days there was nothing to be seen in the liquid in flask A, a strong development of mycoderma in flask B, and a less strong in flask C. This experiment then shows that *Mycoderma aceti* lives at the cost of the acetic acid already formed, and not on the alcohol; that the appearance of mycoderma in wine is rather a consequence than the cause of the chemical decomposition, and that boric acid, if it retards the development of mycoderma, has not the power to prevent it in solutions which contain acetic acid ready formed.

J. K. C.

**Nutrition of the Drosera.** By E. REGEL (*Bied. Centr.*, 1880, 482).—Contrary to Rees and Darwin, the author finds that these plants thrive best when not treated with animal food, and is of opinion that their sustenance is properly derived through the roots.

J. K. C.

**Loss of Dried Substance in Plants during Ripening.** By MARIE-DAVY and others (*Bied. Centr.*, 1880, 440—441).—The authors have observed this fact in connection with wheat, barley, sugar-canes, &c., and concur in the opinion that during the ripening period the plant expels through its roots a certain quantity of superfluous material.

J. K. C.

**Chemical Changes in Frozen and Rotten Potatoes.** By H. CZUBATA (*Bied. Centr.*, 1880, 472—474).—It appears that by freezing, the amount of sugar in the tuber is doubled, starch undergoing a corresponding diminution, while part of the protein passes from the coagulable to the soluble form. During the process of rotting, the potato loses half its nitrogenous constituents and the whole of the sugar.

J. K. C.

**Digestibility and Nutritive Value of Acorns.** By H. WEISKE, G. KENNEPOLL, and B. SCHULZE (*Bied. Centr.*, 1880, 431—434).—As fodder for pigs, acorns have been found very beneficial. The object of the authors was to ascertain their value as bye-fodder in conjunction with hay in the case of sheep. Their experiments show that acorns tend to lessen the digestibility of hay in the same manner as bean and starch meal, whilst alone they have no special value and belong to the class of foods poor in nitrogen, such as potatoes and turnips.

J. K. C.

**Methods proposed for Cleansing Lupines.** By E. WILDT (*Bied. Centr.*, 1880, 434—436).—The bitter taste and poisonous qualities of lupines, due to the presence of alkaloids, prevent their use as fodder. Several methods of removing these alkaloids have been sug-

gested: washing with dilute acid removes them entirely, but the nutritive value of the plants is very much diminished by the process; washing with soda is not sufficient to remove the alkaloids, and the same may be said of the use of water alone; and up to the present no satisfactory process has been discovered.

J. K. C.

**Cultivation of Beetroot.** By L. VILMORIN (*Bied. Centr.*, 1880, 437—439).—Experiments were made with the view of ascertaining the effect of deep ploughing on the yield of beetroot crops. The results showed that deep ploughing has a very favourable influence on the quantity of the crop, but in order to ensure the best quality the plants must be sown near together.

J. K. C.

**Permeability of Soil for Air.** By F. RENK (*Zeitschr. Biologie*, 15, 205—242).—After discussing the importance of the question, the difficulty of the inquiry from the very various considerations it involves; and referring to the work of other experimenters on the subject, the author proceeds to describe his method of experimenting. Munich gravel was the material used, and this was divided first into sand and gravel, and each further subdivided into coarse, medium, and fine by sifting. Tin cylinders, closed at the end by wire gauze of various fineness (the advantages of gauze over wool for this purpose are dwelt upon) were used to contain the material. These cylinders measured 25 cm. to 45 cm. by 5 cm., and were fitted with arrangements for passing the air through them. The size is insisted on, as a closer resemblance to the natural state of things is thereby attained, because the space between any given series of particles and the side of the vessel is greater than the intervals between the particles themselves when closely packed, and this error is the less the larger the containing vessel be, within limits. A gasometer was used for containing the air and an ordinary good gas meter for measuring. Each experiment lasted 1 minute, with very dense material 10 minutes. Two lengthy tables of results are given: No. 1 showing the number of litres of air passed per minute under various pressures given in mm. of water, No. 2 shows the actual amount passed during fixed times and under fixed pressures. Coarse sand and gravel show an exception to the rule that the amount of air passed varies as the pressure.

From the first series of experiments, the author concludes that when air under pressure streams through a porous material the volumes of air passed through are proportional to the variations of pressure so long as the rate of flow is not more than 0.062 meter per second; if this limit is passed, the volume of air increases in a smaller ratio than the pressure, and the proportion diminishes, the greater the speed of the stream of air.

The next point taken up is the effect of varying the thickness of the layer of soil, and from his experiments the author concludes that when air under equal pressures passes through layers of homogeneous materials of different thicknesses the quantity passed through is proportional to the thickness of the layers provided the rate of flow does not exceed 0.062 meter per second; at greater rates, it diminishes in smaller proportion as the thickness of the layer diminishes.



Next the effect of varying porosity is considered. The difficulty of determining porosity is discussed and author's method described, which is as follows:—A cylinder of known volume is filled with the material by shaking, pressing, and hammering, and then turning the contents into a measuring glass half full of water and reading off the amount of absorption which takes place. This part of the subject requires consideration under two heads:—1stly, where the total porosity of the specimens is equal, but the width of the pores is variable; and 2ndly, where the width of the pores is equal but the total volumes variable.

The results are given in the following table, which shows the varying resistance to the passage of air very markedly:—

TABLE.

|                          | Gravel.   |           | Sand.     |           |           |
|--------------------------|-----------|-----------|-----------|-----------|-----------|
|                          | Medium.   | Fine.     | Coarse.   | Medium.   | Fine.     |
| Number of experiments.   | 86        | 87        | 88        | 89        | 90        |
| Volume of cylinder....   | 981       | 981       | 981       | 981       | 981       |
|                          | grams.    | grams.    | grams.    | grams.    | grams.    |
| Weight of material....   | 1638      | 1638      | 1638      | 1463      | 1463      |
|                          | per cent. | per cent. | per cent. | per cent. | per cent. |
| Estimated vol. of pores  | 37.9      | 37.9      | 37.9      | 55.5      | 55.5      |
| Pressure in mm. of water | 20        | 20        | 20        | 20        | 20        |
| Air passed (liters) .... | 15.54     | 6.91      | 1.28      | 0.112     | 0.00133   |

After referring to the results of other experimenters (Gueront, *Compt. rend.*, 75; Schürmann and O. E. Meyer) on the passage of gases through capillary tubes and similar resistances, he concludes that the width of the pores has an important influence on the total permeability of the soil, to this extent: that by comparison of two specimens of soil of equal volume, but of which the individual particles were of different sizes, the pore volume and transverse sections equal, and under equal pressures, it was found that the quantity of air passed through the one might be 20,000 times greater than the quantity passed through the other in the same time.

When the pores are of equal size, but the total pore volume varies, the quantity of air which passes varies as the area of section of the containing vessels.

The details of further experiments with loosely packed and wet soils are given, and the author then proceeds to summarise the results of all the experiments as follows:—When air under pressure flows through a soil, the quantity which passes through is directly proportional to the pressure and inversely proportional to the thickness of the stratum, provided only that the rate of flow does not exceed 0.062 meter per second. If this limit be passed, the proportion changes and the volume of air passing through diminishes in a smaller ratio

as the pressure diminishes and the thickness of the stratum increases, and *vice versa*.

Porosity, by which only one property of a body is understood, viz., the existence of spaces throughout its apparent mass, has a double influence. 1st, in different soils whose pores are of equal dimensions, under equal pressure, the volume of air passed through is proportional to the total pore volume; and 2ndly, when the pores are of different dimensions, but the total pore volume is the same, it is possible in extreme cases, that the quantity of air passing through one sample may be 20,000 times greater than through another.

An alteration of these factors occurs when a soil is loosened, for then not only the size of the individual spaces, but also their total volume, is increased; with fine soils, i.e., soils with fine pores, a *relatively* greater permeability results than with soils whose pores are larger.

The wetting of soils by rain has, according to the width of the pores, a very different effect; soils whose pores are large may be but slightly affected, whereas soils with fine pores may be rendered practically impermeable.

When a soil freezes, its permeability is lowered, and this not only in consequence of the expansion of the water by frost, but also and chiefly because the water when frozen is no longer moveable in the pores.

W. N.

**Influence of Shade on the Amount of Carbonic Anhydride in the Air of the Soil.** By E. WOLLNY (*Bied. Centr.*, 1880, 402—405).—Three zinc cylinders were filled to the height of half a meter with damp sandy soil into which a glass tube was sunk for half the depth in order to draw off the air: one cylinder was covered with grass, another with straw, and the third was left open. Experiments carried on during the warmer season of the year showed that during this time the air of soil shaded by green plants contained much less carbonic anhydride than when the soil was covered by dead plants or left open, whereas the opposite is the case during the colder seasons. The author has formerly proved that the air under growing plants during warm weather is both colder and drier than that which is not so shaded, and in this we have the reason why less carbonic anhydride is present. The author finds the amount of carbonic anhydride to diminish in proportion to the density of the green plants.

J. K. C.

**Difference between Loam and Clay.** (*Bied. Centr.*, 1880, 480—481).—By a process of elutriation, the very fine parts were separated from the coarser and subjected to a quantitative analysis; it was found that the chief difference between loam and clay consisted in the fine portions of the latter containing 13 to 14 per cent. of calcium carbonate, of which the loam contained none, but was correspondingly richer in silicates.

J. K. C.

**Permeation of Vegetable Matter by Water.** By W. RIGLER (*Bied. Centr.*, 1880, 406—408).—A gentle stream of water was allowed to play on beach and pine litter and on sphagnum; the amount of water which trickled through was measured. It was found that a

downfall of 10 mm. of water was reduced on the first day to 8 by beech straw, to 8·8 by the pine, and to 4·3 mm. by the sphagnum. Perfectly dry straw does not absorb water very quickly, a certain proportion of moisture being necessary to give the most favourable conditions. J. K. C.

**The Best Mode of Applying Artificial Manure to Potatoes.** By M. MARCKEE (*Bied. Centr.*, 1880, 409—418).—Experiments were carried on for four years with several different kinds of potatoes, and in soil of very varied quality, to ascertain what kinds of artificial manures were most suitable and in what proportions they should be used, whether alone or in combination with other kinds of dung. When artificial manures were used alone, the best effect was produced by a mixture of Chili saltpetre and Baker superphosphate in the proportion of one of the former to two of the latter. The saltpetre by itself was productive of very good results, but the use of superphosphate alone was found to be a failure. In combination, however, with stable manure, each separately produced about the same effect, but when used together in the same proportions as given before, their influence on the crop was still more favourable. Salts of ammonia were of no use, the nitrogen being apparently not absorbed until oxidised to nitric acid. J. K. C.

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### Analytical Chemistry.

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**Meyer's Vapour-density Determinations.** By L. MEYER (*Ber.*, 13, 991—992).—The author describes an arrangement by which the error described by V. Meyer (*Ber.*, 13, 813—814) may be avoided, which results from the introduction of air into the apparatus when the bottle containing the substance is brought into the apparatus. The arrangement consists in closing the apparatus by a caoutchouc stopper, in which fits a glass tube closed at the upper end and open at the lower end; into this the tube containing the substance under experiment is introduced. It is held in its position by means of a piece of iron wire passing through the caoutchouc stopper, and bent below so as to form a support for the tube, whilst above it is bent at right angles so to form a handle, by which at the desired time it may be turned round. In this way the support can be removed from below the tube, when it drops down into the heated part of the apparatus. To avoid the water being carried over through the side tube whilst the tube is falling, a small bulb is blown on the side tube.

P. P. B.

**New Alkalimetric Method for Estimating Phosphoric Acid.** By O. SCHLICKUM (*Arch. Pharm.* [3], 15, 325—334).—When litmus is used as an indicator during the addition of an alkaline hydrate to phosphoric acid, the neutral point is reached as soon as the hydrogen of the acid is half replaced by metal.

If tincture of cochineal is employed, the yellow colour imparted to it by the acid changes to violet-red when one-third of the hydrogen of the acid is replaced by the metal, that is, when a monometallic phosphate is formed. Cochineal therefore serves to indicate the stage at which phosphoric acid is one-third saturated; the presence of other acids does not interfere, since they are neutralised by the alkali before the phosphoric acid: hence when phosphates are to be estimated, normal nitric acid is added and titrated.

Phosphoric acid in the presence of magnesium sulphate can be precipitated as  $MgNH_4PO_4$  by addition of normal ammonia, and each molecule of acid requires 3 mols. of ammonia for its complete precipitation: 1 mol. of a monometallic phosphate similarly requires 2 mols. ammonia. The end of the precipitation process can be judged by litmus, which remains violet-red until a drop of ammonia in excess is added, which turns it blue: if excess of ammonia has been added it may be titrated back by standard acid after separating the precipitate.

When it is to be estimated by the following process, phosphoric acid must be present either as free acid or as a monometallic salt: all other phosphates may be converted into the monometallic salt by addition of nitric or hydrochloric acid until cochineal tincture is turned yellow.

The process consists in adding sufficient magnesium sulphate and some tincture of litmus, and then running in normal ammonium hydrate until no further precipitate forms and the litmus changes from violet-red to blue: towards the end of the reaction, the precipitate settles very rapidly, and it is necessary to allow a few seconds between each addition of ammonia to complete the change. As soon as the addition of the last drop of ammonia has produced no change of colour the volume of ammonia used is read off. To calculate the amount of phosphoric acid present, it is only necessary to multiply by the factor 0.098 one-third the number of cubic centimeters of ammonia solution used if free phosphoric acid was being titrated, and one-half the number of cubic centimeters if a monometallic phosphate was present. Excess of ammonia may be titrated back with normal acid, after first separating the liquid from the precipitate.

If calcium is present, it must either be removed or precipitated as sulphate by heating nearly to boiling with sodium sulphate and allowing it to stand for half an hour: the solution containing a little dissolved calcium sulphate may be poured off and mixed with magnesium sulphate and litmus, or the removal of the precipitate may be neglected. It is, however, necessary that the calcium phosphate should first be converted into the monocalcium phosphate by normal nitric acid and cochineal, or by normal ammonia as the case may be, and the quantity of either of these normal solutions employed measures the amount of calcium present.

F. C.

**Action of Ammonium Citrate on Phosphates.** By A. GRUPE and B. TOLLENS (*Ber.*, 13, 1267—1270).—Dicalcium phosphate dissolves in an alkaline solution of ammonium citrate with the formation of ammonium phosphate and calcium citrate, the latter being soluble in an excess of the ammonium salt. Tricalcic phosphate is less solu-

ble than the diphosphate in ammonium citrate. In order to estimate the phosphoric acid in this solution, three times the amount of magnesia mixture required by theory should be added; a larger excess is to be avoided. The precipitate invariably contains lime, which can be removed by dissolving the washed precipitate in hydrochloric acid and reprecipitating with ammonia. W. C. W.

**Valuation of Zinc and Zinc-dust.** By F. BEILSTEIN and L. JAWEIN (*Ber.*, 13, 947—951).—The samples of zinc or zinc-dust are dissolved in hydrochloric acid, the hydrogen liberated is collected in an apparatus from which it expels water, and from the weight of the latter the hydrogen liberated is calculated. For a description of the apparatus and the precautions necessary to obtain accurate results, the original must be consulted. P. P. B.

**Valuation of Copper for Roofing.** By A. MÜLLER (*Ber.*, 13, 1014—1016).—The author proposes submitting for equal length of time pieces of sheet copper of equal size, to the action of hydrochloric acid fumes, then to a solution of hydrochloric acid of 15—20 per cent., and after exposure to the air, dipping them into nitric acid of about 10 per cent.  $N_2O_5$ . Different varieties of copper are variously attacked; and when their surfaces are examined microscopically data are obtained sufficient to form an opinion as to the suitability of the copper for roofing. Some samples are attacked uniformly over the whole surface, giving a roughened surface only, whilst others are corroded deeply here and there; the latter kinds would be unsuitable for roofing purposes. P. P. B.

**Quantitative Determination of Acetone in Methyl Alcohol.** By G. KRÄMER (*Ber.*, 13, 1000—1005).—The method consists in weighing the iodoform obtained by shaking up 1 c.c. of the alcohol with 10 c.c. of double normal soda solution and 5 c.c. of double normal iodine solution. To remove the iodoform, 10 c.c. of ether free from alcohol are shaken up with the mixture, and an aliquot part of the ether drawn off and evaporated on a weighed watch-glass. The increase of weight of the watch-glass gives the iodoform contained in the ether, from which the amount of acetone may be calculated.

Ethyl alcohol, acetic acid, and propyl alcohol, when treated as above, give no iodoform, whereas isopropyl alcohol yields iodoform. Aldehyde does not give the theoretical amount; ketones containing methyl groups, e.g., methyl ethyl ketone, methyl hexyl and methyl phenyl ketones also yield iodoform, and an acid containing 1 atom of carbon less than the ketone. P. P. B.

**Estimation of Starch in Sausages.** By H. FRICKLINGER (*Arch. Pharm.* [3], 15, 234—235).—The presence of starch, introduced into meat sausages as bread or wheaten flour, is an adulteration. Its amount has usually been determined by conversion into sugar by digestion with dilute sulphuric acid, and then titrating the sugar with copper solution: the starch is considered to be entirely converted when iodine solution imparts no blue or violet coloration. The author

points out that the intermediate product, dextrin, has no action on starch, and hence the iodine reaction cannot be employed: he found that from one-third to one-half of the starch is not found if the iodine test is used. The following method is recommended: A known weight of the sausage in thin slices is digested at  $100^{\circ}$  with water containing 5 per cent. of sulphuric acid, until a filtered portion of the liquid yields no further precipitate with alcohol. The liquid is filtered, the residue well washed, and after making the solution alkaline with soda, the sugar is titrated with copper solution. F. C.

**Comparative Examination of the most important kinds of Commercial Gum Arabic.** By E. MASING (*Arch. Pharm.* [3], 15, 216—234).—10 per cent. solutions of the gums clarified by standing were usually employed, but in some cases dilution down to 5 per cent. was necessary, owing to the liquid being too tenacious: clarification was seldom necessary. The following reagents were employed, and the solubility of the precipitate in excess of the reagents was tested by pouring 2 c.c. of the gum solution into a test-tube, adding to this first an equal volume of the reagent, then an additional 2 volumes and shaking well:—

1. *The solubility* was determined by pouring 25 c.c. of water upon 0.5 gram of the gum, and constantly shaking for 24 hours in a closed vessel; the residue removed by filtration was dried at  $110^{\circ}$  C.

2. *The moisture* was estimated by drying the gum at  $110^{\circ}$  C.

3. *The ash* was obtained from 2 to 5 grams of air-dried gum, and its alkalinity was titrated.

4. *Potassium silicate* solution, made by diluting 1 part of thick water-glass with 20 parts of water, precipitated almost all the gum solutions.

5. *Potassium stannate*, as 2 per cent. solution, also affected all the gum solutions except one.

6. *Lead acetate* reacted, with one exception, on all the solutions.

7. *Neutral aluminium sulphate* in 10 per cent. solution only precipitated two gum solutions: but the precipitate obtained from other samples, on the further addition of potassium hydrate (1.13 sp. gr.), was examined as regards its solubility in excess of the caustic alkali.

8. *Neutral copper acetate* in cold saturated solution, *neutral lead acetate* in 10 per cent. solution, and *ferric chloride* solution of 1.2 sp. gr. were indifferent to almost all the gum solutions.

The reaction of most gum solutions was feebly acid. Starch was estimated microscopically in the deposit from the water solution by moistening it with a 1 per cent. aqueous iodine solution.

The author concludes from the examination of a large number of gums, the results of which are tabulated, that although different kinds of gum show differences when thus tested, the source of the gum can seldom be inferred from such an examination. The value of the gum is better judged from its solubility than from its colour: the percentage of ash seldom varies beyond narrow limits, but the alkalinity of the ash is much more variable; the alkalinity was usually entirely or mainly due to lime, and potash was seldom present in any quantity. The ash was invariably soluble in dilute hydrochloric acid, and any

quantity of insoluble residue would therefore indicate the presence of sand or other insoluble substances. The differences in behaviour shown by the different kinds of gum towards the same reagent probably indicates the existence of different modifications of arabic acid.

F. C.

**Observations on Milk.** By B. OHM (*Arch. Pharm.* [3], 15, 211).—When powdered well-burnt gypsum is mixed with milk to a stiff paste, the time required for its setting serves as a measure of the quality of the milk and of the quantity of water added as an adulterant.

Milk of 1.030 sp. gr. at 15° C. was mixed with about 30 grams of gypsum, and set in 10 hours; after the addition of 25 per cent. of water 2 hours only were required, with 50 per cent. 1½ hours, and with 75 per cent. only 40 minutes.

Milk skimmed after standing for 24 hours and of 1.033 sp. gr., when mixed with gypsum set in 4 hours, with 50 per cent. of water it set in 1 hour, and with 75 per cent. in about half an hour.

If the milk is warmed it sets more rapidly. The mass after setting can be used for further examination.

F. C.

**Taking Samples of Milk.** By C. WERKOWITSCH and V. KLENZE (*Bied. Centr.*, 1880, 469—470).—The milk should be well stirred, and a sample taken from the middle by inserting an inverted beaker in the liquid, reversing and drawing it out.

J. K. C.

**Analysis of Milk.** By E. MARCHAND (*Bied. Centr.*, 1880, 466—468).—The great variations in the analyses of milk by different chemists are due, according to the author, to the abnormal conditions of the cow, the various times of milking, or defective methods of analysis. Only in the case of the fat does the quantity show any great variation (2.7 to 8.2 per cent.). To estimate the fat, milk is treated with moderately dilute acetic acid, which dissolves the casein, and allows the fat to be filtered off; or the fat is dissolved out by shaking with ether.

J. K. C.

**Analysis of Milk.** By H. VOGEL (*Dingl. polyt. J.*, 237, 59—61).—The author recommends weighing the milk in a closed tube, as an appreciable error results from weighing it in an open basin. To estimate solid residue and fat, he uses a tinned-iron boat made to fit Soxhlet's extraction apparatus, and stirs up the milk, after the addition of sand, during evaporation. Feeding cattle with green fodder caused no appreciable change in the composition of the milk. The author thinks that the number, 9, fixed by English analysts as a minimum for solids, not fat, is too high; he would prefer 8. Judged by the former standard, all the samples in his district would be condemned as watered.

J. T.

**Analysis of Butter.** By E. MEISSEL (*Bied. Centr.*, 1880, 471—472).—5 grams of well-washed butter are dissolved in alcohol and saponified with caustic potash. After the alcohol has been evaporated, the soapy liquid is distilled with dilute sulphuric acid, and the distillate titrated with decinormal potash solution. The number of cubic

centimeters of potash-ley used is a test of the purity of the butter, and should not be less than 26. J. K. C.

**Estimation of Albumin.** By H. P. ARMSBY (*Bied. Centr.*, 1880, 449—450).—The author found that watery extracts of hay were rendered quite free from albumin by means of Sestini's and Ritthausen's methods. J. K. C.

**Detection of Paralbumin.** By VULPIUS (*Arch. Pharm.* [3], 15, 307—310).—The test for paralbumin in certain accumulations of fluid in the body is of importance, since its result assists the medical man in forming an opinion as to the source of the liquid. The author recommends that the test be made as follows:—100 grams weight of the clear fluid is diluted with six times its weight of water; if the liquid will not pass through the filter, it is diluted with half the above quantity of water before filtration, and if filtration is then found to be impossible, it must be allowed to stand until the largest particles have settled. Washed carbonic anhydride is then passed through the liquid for several hours. The presence of paralbumin is shown by the appearance of a turbidity which gradually subsides as a white flocculent precipitate. The above dilution is absolutely necessary to secure the ready and full precipitation of paralbumin.

Another method consists in adding three volumes of absolute alcohol to the liquid, collecting the precipitate by filtration after twenty-four hours, and washing it with absolute alcohol. After being pressed between filter-paper the precipitate is warmed at 50—60° for several hours with fifty times its weight of distilled water: any paralbumin present passes into solution and may be detected by adding thousand-fold diluted acetic acid, by which paralbumin is precipitated but is redissolved by excess. Paralbumin is further distinguishable from metalbumin by yielding no precipitate with magnesium sulphate.

F. C.

**Determination of Sap in Beet.** By A. GAWALOWSKI (*Bied. Centr.*, 1880, 465—466).—The author describes a slight modification of Stammer's process of estimating the quantity of sap in beetroot.

J. K. C.

**Opium Testing.** By E. MYLIUS (*Arch. Pharm.* [3], 15, 310—324). The author has subjected Flückiger's method to an experimental criticism, and publishes the results arrived at. In preparing the extract, six hours' maceration with water was found to be insufficient, and the writer recommends twelve hours' treatment: in this way nearly the whole of the soluble matter may be extracted. He also determined the sp. gr. of aqueous extracts of opium at 17°, and tabulated the results. By reference to the table, the percentage of extracted matter can be at once found when its sp. gr. has been taken: this method is an extremely simple one for estimating the value of opium, and dispenses with the moisture determination.

The percentage of extracted matter given by Flückiger is, in round numbers, 60; this number is higher than that usually accepted on previous authority.

Flückiger's method was also tested by applying it to the estimation



of known quantities of pure morphine. It was found that the results were always too low, and that this was due to the solubility of the morphine in the mixture of alcohol and ether. The amount of this solubility was determined, and it was shown that by adding 0.088 gram to the weight of morphine obtained by Flückiger's process, the determinations became absolutely, and not merely relatively, correct.

One other improvement suggested is the weighing of the morphine on the filter instead of in the flask. The difficulty of perfectly drying the substance and interior of the flask is considerable. The author prefers to remove the larger crystals to a filter, and then to detach the crystals from the interior of the flask by a glass rod or by shaking a piece of platinum-foil round the interior, and to rinse these crystals on the filter with some of the filtrate. The crystals are then washed with 10 grams of a mixture of equal volumes of ether and alcohol, and the filter gently pressed between folds of filter-paper until freed from the mother-liquor: after having been dried at 100° for half an hour, the filter is exposed to the air for half an hour, when the paper absorbs fully its hygroscopic water; it is then weighed with the crystals, and, finally, the crystals are removed by a small brush and by tapping, and the filter is weighed.

F. C.

## Technical Chemistry.

**Purification of Refuse Water.** By E. REICHARDT (*Arch. Pharm.* [3], 15, 236—246).—The author enforces the necessity of purifying all refuse liquids before they are admitted into streams, lakes, and ponds, both for sanitary reasons and to prevent injury to fish.

*Subsidence.*—This process, which clarifies the glacier stream during its passage through a lake, serves to remove harmful matters from many refuse liquids. Two or three subsidence ponds, in which the growth of water-plants may be encouraged, are frequently all that is necessary to prevent the contamination of a stream: the sediment periodically removed is in many cases valuable as manure. In some cases the effluent may be passed through a series of tanks formed by digging holes in the ground and protecting the sides with masonry, cement, or pitch: the waste water entering each by a pipe directed downwards, below the mouth of which the stream meets a flat stone, and is thus prevented from stirring up the lower part of the liquid: from the last of these tanks the discharge pipe may pass upwards from beneath the surface of the liquid so as to prevent the escape of floating films of oil and petroleum.

*Chemical Purification.*—Dissolved impurities, which cannot be removed by subsidence alone, frequently require to be chemically precipitated. Before subjecting water to chemical treatment, the manufacturer should be careful to treat only that which is impure, and to turn direct into the stream all such water as has been used for driving machinery or for other cleanly purposes. Care should also be

taken that the volume of water to be purified should be made as small as possible. No water containing free acid or alkali should enter a stream until it has been neutralised, as the salts are less injurious than the free acid or alkali: it will generally, however, be found that the stronger washing-waters may with advantage be kept and their contents worked up.

Lime and chalk are the most generally useful precipitants and purifiers: by their means not only may acid liquids be neutralised, but many colours and albuminous substances may be rendered insoluble. Alum and other substances may sometimes be used with lime. Lime in excess is mixed with the refuse in the first of the above-mentioned tanks: after subsidence, the clear effluent will still contain dissolved lime, which is injurious to fish and must be separated by exposure to the air in larger ponds. The lime sediments can be used for manure.

In all cases the purified effluent water should enter the stream by pipes which discharge it upwards from near the bottom and middle of the stream; this secures rapid admixture with a large quantity of stream-water.

Details are given of the number of works which discharged impure waste water into running water in Saxony in the year 1877: the majority were colour-, bleach-, and woollen-works. Breweries seldom offended; the author finds that the brewery waste contains chiefly albuminous bodies, which can be almost completely removed by lime.

F. C.

**Occurrence of Free Sulphur in the Dry Distillation of Tar.** By A. KEHLSTADT (*Ber.*, 13, 1345—1347).—A deposit in the passage connecting the condensers at a tar distillery with the chimney was found to consist chiefly of sulphur, which probably owed its origin to the mutual decomposition of sulphurous oxide and sulphuretted hydrogen.

W. C. W.

**Magnesium and Calcium Compounds as Refractory and Dephosphorising Materials.** By K. BISCHOF (*Dingl. polyt. J.*, 237, 51—59, 136—143).—The author mentions the various compounds hitherto proposed for basic refractory bricks, linings, &c. He then examines the behaviour of three of the best mixtures proposed by S. G. Thomas.

|                     | (a.)<br>Parts. |  | (b.)<br>Parts. | (c.)<br>Parts. |
|---------------------|----------------|--|----------------|----------------|
| CaO, pure . . . . . | 85             | CaO . . . . .                            | 80.0           | 58.5           |
| Clay (Grünstadt)..  | 5              | MgO . . . . .                            | 5.5            | 30.5           |
|                     |                | Al <sub>2</sub> O <sub>3</sub> . . . . . | 4.0            | 2.5            |
|                     |                | Fe oxide . . . .                         | 1.5            | 1.5            |
|                     |                | SiO <sub>2</sub> . . . . .               | 8.0            | 7.0            |

*b* is a mixture given for bricks; *c* is the best mixture for the outer lining of converters.

*a* at the fusing point of cast-iron formed a yellowish smooth mass like sealing-wax, with compact fracture; *b* gave a rough, brownish, somewhat granular mass, with a cellular and cracky fracture; *c*, like

*b*, but darker; *a* bit dropped from its platinum support to a clay support beneath seemed fused to the latter. At the fusing point of cast-steel, *a* was darker, *b* and *c* as above, but with lava-like fractures. At the melting point of bar-iron, *a* formed a light yellow enamel; *b* was yellowish-brown, partly fused to a yellow enamel; and *c* was brownish-yellow, beginning to form an enamel. *a*, the most fusible, is also most complex in composition; most of its proximate components are also in combination to begin with. With *b* and *c* the fusibility increases with the increase in amount of  $\text{SiO}_2$ . Replacing the  $\text{CaO}$  in *a* by 85 parts of  $\text{MgO}$ , a mixture decidedly more refractory resulted; near the fusing point of bar-iron it baked together only, whilst the former became enamel-like. Other experiments confirmed the conclusion that  $\text{MgO}$  with clay gives more refractory mixtures than  $\text{CaO}$  does. The assertion that  $\text{MgO}$  bricks formed of these compounds must be burnt at a temperature near the fusing point of platinum must be taken as a very rough approximation only, as they would be quite fluid at that temperature.

The author also examined the behaviour of the proximate constituents, magnesia, lime, alumina, iron oxide, silica, and phosphoric anhydride at different temperatures, to throw some light on the behaviour of the compounds. Chemically pure magnesia heated to nearly the melting point of platinum becomes compacted on the surface, but is infusible, even when in contact with refractory clay; at the melting point of platinum a test fused to a grey mass. Lime at the melting point of bar-iron forms a skin; near the melting point of platinum, it melts when in contact with clay. Pure alumina is perfectly infusible at the melting point of platinum. Pure iron oxide gives a fused product on platinum at the melting point of bar-iron. Silica is more fusible at the melting point of bar-iron than magnesia. It bears heating to near the melting point of platinum on a clay support. Phosphoric anhydride fuses at a comparatively low temperature. Compounds of magnesia and silica slowly increase in fusibility with the amount of silica until a great excess has been added. With equal parts of each, perfect fusion takes place at the melting point of bar-iron. Magnesia with phosphoric anhydride gives much more fusible compounds than with silica, and the fusibility increases with the amount of anhydride present. Magnesia and alumina compounds, either on a platinum or on a clay support, remain almost unchanged at the melting point of bar-iron. Magnesia and lime compounds at the melting point of bar-iron do not fuse, but those with a preponderance of lime show signs of incipient fusion. All the mixtures of magnesia with iron oxide were infusible at the melting point of silver; but at the melting point of bar-iron all fused. The fusibility increases with the amount of oxide.

Lime and silica form very much more fusible compounds than the corresponding magnesia and silica ones. The same may be said of lime and phosphoric anhydride. Lime forms much more fusible compounds with alumina than magnesia does. This appears even in compounds containing as much as 3 to 1 of alumina to lime. Similarly lime and iron oxide are more fusible than the magnesia mixture.

J. T.

**Enamelled Cast-iron Vessels.** By W. BIRSCH (*Dingl. polyt. J.*, 237, 78).—After pickling and cleaning the vessels, they are covered with a ground made as follows:—Quartz, 50; fluorspar, 7·5; borax, 22·5 are fused together. Of this, 16 parts, 6·5 to 12·5 quartz, 4 to 6·5 of clay, 0·5 borax, are ground in wet mill, with addition of 2·5 clay and 0·66 borax. This is laid on and burnt, forming a yellowish-brown mass. For the outer coating, 2·5 powdered fluorspar, 1 zinc white, 4·75 tin oxide, 0·75 bone ash, and 0·03 to 0·05 smalt are well mixed. Of this 9 kilos. are mixed with 16 of finely ground fluorspar, 9·5 borax, 3·25 soda, 1·25—1·5 nitre, and the whole fused together. The product is powdered, and 30 kilos. of it wet ground with six cups of about 140 c.c. of white clay and 0·3 zinc oxide. This is laid on and burnt.  
J. T.

**Alcohol from Potatoes.** (*Bied. Centr.*, 1880, 485).—Comparative experiments on mashing potatoes with sulphuric acid and with malt showed that the yield of alcohol obtained by means of the latter was very little greater than that obtained by boiling with sulphuric acid at the ordinary pressure.  
J. K. C.

**Analyses of Tokay Wines.** (*Bied. Centr.*, 1880, 485).—In six samples of wine the percentage of alcohol varied from 7·8 to 17·6; of solids from 27·1 to 8·4; and of sugar from 23·4 to 6·1.  
J. K. C.

**Analyses of Hamburg Beer.** By NIEDERSTADT (*Bied. Centr.*, 1880, 484).—As a mean of 28 samples, the percentage of alcohol was found to be 4·3, and of extract 5·7.  
J. K. C.

**Extraction of Malt.** (*Bied. Centr.*, 1880, 485).—Several samples of grains were analysed, and it was found that about 7 per cent. of the extractive matter was still present in the grains.  
J. K. C.

**Experiments on Various Kinds of Yeast.** By A. RIEBE (*Bied. Centr.*, 1880, 477—478).—These experiments were carried out in mashes of molasses. Yeast was found to be most active when it had previously been allowed to stand with potato mash. An attempt was made to substitute fresh malt yeast for dry malt yeast, which, however, was not successful.  
J. K. C.

**Estimation of the Value of Raw Material in the Preparation of Yeast.** By HEINZELMANN (*Bied. Centr.*, 1880, 475—476).—The yeast-producing power of grain is not proportionate to the quantity of nitrogen it contains, but to the amount of soluble protein. This is a very variable quantity, rye containing from 30 to 50 per cent., and maize only 10 per cent. of its protein soluble in water at 65° C., which is the most suitable temperature for mashing the grain.  
J. K. C.

**Inversion of Beet-sugar for Wine.** By W. EUGLING (*Bied. Centr.*, 1880, 486).—Sulphuric, phosphoric, and tartaric acids were used in the inversion of beet-sugar, sulphuric acid being the quickest,

and tartaric acid the slowest in its operation. The inverted sugar was then used for the preparation of after-wine, being mixed with pressed grapes and allowed to ferment. The best wine was obtained from the sugar inverted by means of phosphoric acid. J. K. C.

**Sugar from the Stems of Maize and Sorgho.** By P. COLLIER (*Bied. Centr.*, 1880, 461—462).—The author found that sugar could easily be obtained, and in considerable quantity, from the sap of the stems of maize and sorgho, the sap yielding about 15 per cent. of syrup. J. K. C.

**Action of Lime on Solutions of Sugar.** By F. DESOR (*Bied. Centr.*, 1880, 464—465).—If lime-water be added to a solution of sugar, the rotatory power of the latter is diminished, although the diminution does not seem to follow any law. Addition of acetic acid restores the rotatory power. J. K. C.

**Gypsum in the Manufacture of Sugar.** By A. v. WACHTEL (*Bied. Centr.*, 1880, 463).—The author attributes the presence of alkaline sulphates found in sugar to the presence of gypsum in the water used in sugar works. J. K. C.

**Certain Properties of Bone Charcoal.** By H. PELLER (*Bied. Centr.*, 1880, 463—464).—Bone-black will absorb lime from sugar solutions, and lime salts equally well if an alkali be present. Potash salts are also easily absorbed, especially in the presence of lime. J. K. C.

**Influence of Steaming on Starch.** By M. STUMPF (*Bied. Centr.*, 1880, 457—459).—A mixture of one part of starch to four of water, when heated at 130° C. under pressure, becomes a homogeneous liquid, the starch, however, partially separating out on cooling. After four hours' heating, the author found that 20 per cent. of the starch had been converted into sugar. When only half the quantity of water is used, three hours' heating at a temperature of 125° under a pressure of 2½ atmospheres, is necessary to reduce the whole to a liquid. When the temperature is raised to 140—150° over 70 per cent. of the starch may be converted into sugar. J. K. C.

**Notes on Milking.** (*Bied. Centr.*, 1880, 232—233.)—C. J. Hisein advocates the use of a strict record of trial milkings,\* as not only useful to detect bad milkers amongst the cows, but as a guide to the results of the fodder, and enabling the farmer to better estimate his profits. B. Martiny and W. Fleischmann give examples of the great errors which may occur by taking trial milkings from a single cow in a herd, especially if the trials are only made monthly: trustworthy estimates of the yield of single cows can only be had if the trials are made weekly. J. F.

**Experiments with Milk Cooling Apparatus.** (*Bied. Centr.*,

\* Such trial milkings are always followed by analyses.

1880, 214—216.)—The object of the experiments was to determine whether it is more profitable before churning to put the milk fresh from the cow into the ice-water of the Swart's system, or to cool it previously in the Laurence cooling apparatus. The results show that when the milk is cooled too much, the yield of cream diminishes. However, if the milk is not cooled too much, and is placed in ice immediately after a slight cooling, there is very little appreciable loss. It is, however, different if the milk is left at rest for a few minutes before being transferred to ice, the decrease in fat being then in quite regular proportion to the time allowed to elapse. It is possible, however, to recover the normal amount by rewarming the milk, and then placing it quickly in ice. If the milk is retained at a proper temperature, the yield is not injuriously affected by allowing it to remain 45 minutes previous to placing it in ice.

The writer's theory is that the sudden cooling of the milk first takes effect on the serum, and the fat-globules, before they have time to cool, float to the surface; another theory is, however, proposed by a writer in the *Centralblatt*, that the cooling sets up a current, the motion of which carries the fat to the surface. In any case the experiments recorded are in favour of the Swart's plan.

J. F.

**Supposed Conversion of Albumin into Fat in the Ripening of Roquefort Cheese.** By N. SIEBER (*J. pr. Chem.* [2], 21, 203—221).—Blondeau finds that such a conversion takes place, Brassier (*Ann. Chim. Phys.* [4], 5, 1865) and Alex. Müller (*Jahrs. f. Agri. Ch.*, 1870—72, 246) come to a contrary conclusion, and the results obtained by the latter agree with those of the author. The author severely criticises Blondeau's experiments.

The author's results of the analysis of (1.) Fresh cheese (not salted). (2.) Cheese after remaining in the cellar; and (3.) Very old cheese, are:—

|                       | (1.)  | (2.)  | (3.)  |
|-----------------------|-------|-------|-------|
| Moisture .....        | 49.66 | 36.93 | 23.54 |
| Casein .....          | 13.72 | 5.02  | 8.53  |
| Soluble albumin ..... | 6.93  | 20.77 | 18.47 |
| Fat .....             | 27.41 | 31.23 | 40.13 |
| Ash .....             | 1.74  | 4.78  | 6.27  |
|                       | 99.46 | 98.73 | 96.94 |

The most remarkable change in the ageing of the cheese is the loss of moisture. The increase in fat is only an apparent one, for calculating on the dry substance we have the following percentages for the fat and the albumin (casein + soluble albumin):—

|               | (1.)  | (2.)  | (3.)  |
|---------------|-------|-------|-------|
| Fat .....     | 53.91 | 49.94 | 56.14 |
| Albumin ..... | 40.80 | 40.53 | 37.78 |

The moisture was determined by drying at 115—120°. Blondeau merely dried over sulphuric acid. The fat was determined by extraction with alcohol and ether, the residue free from fat was dissolved

in potash, leaving but little residue, and the filtrate precipitated by dilute acetic acid. This precipitate washed, dried, and weighed is called casein, the total albumin being calculated from the nitrogen determination by combustion with cupric oxide. In the case of the old cheese, under the heading "soluble albumin," the nitrogen from which the "soluble albumin" is calculated exists in part as tyrosine, amido-fatty acids, and ammonium salts. In the old cheese, by operating on half a kilogram, 1.4 per cent. ammonia, and 0.167 per cent. tyrosine were obtained. F. L. T.

**Examination of Dog Biscuit.** By A. MAYER (*Bied. Centr.*, 1880, 233).—A Liverpool firm having introduced this article into commerce, it has been analysed by the author, who found it to yield the following percentage composition:—

| Moisture. | Starch and<br>digestible matter. | Fat. | Albumin. | Cellulose, &c. | Ash. |
|-----------|----------------------------------|------|----------|----------------|------|
| 13        | 45.5                             | 3.6  | 16.1     | 19.3           | 2.5  |

The composition appears similar to that of rye bread, only the fat and albuminoids appear to be derived from slaughter-house refuse; a microscopical investigation does not show the presence of good meat.

J. F.

**Tonga.** By A. W. GERRARD (*Pharm. J. Trans.* [3], 10, 849).—Tonga, a drug obtained from the Fiji Islands, is a mixture of fibrous material, probably a root, and the inner bark of some plants. The bark consists of pectin, glucose, an essential oil and fat; the root contains a volatile alkaloid, probably the active principle, and potassium chloride.

The drug is used as a remedy for neuralgia.

L. T. O'S.

**Deterioration of Library Bindings.** By W. R. NICHOLS (*Chem. News*, 41, 64).—The author's results confirm the generally accepted view that the deterioration of leather bindings is to be mainly traced to the action of sulphuric acid produced by combustion of coal gas. Morocco leather is but little affected; Russia and calf are much acted on; ordinary sheep-skin is also attacked.

M. M. P. M.

**Fruit of *Adansonia Digitata*.** By F. L. SLOCUM (*Pharm. J. Trans.* [3], 10, 816).—The fruit of *Adansonia digitata* contains pectin, grape-sugar, malic acid and potassium, but not a trace of tartaric acid, consequently it is distinct from the "cream of tartar" fruit.

L. T. O'S.

## General and Physical Chemistry.

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**New Methods in Actino-Chemistry.** By A. R. LEEDS (*Chem. News*, 42, 44).—The author confirms his results previously obtained (*Am. J. Sci.*, 1878 and 1879), and also the laws relating to the change of the soluble iodides in presence of actinic rays and dilute acids.

The amount of iodine set free in presence of hydrochloric acid in sunlight is greater by a definite ratio than that liberated by sulphuric acid.  
L. T. O'S.

**Photochemical Behaviour of Silver Bromide in presence of Gelatin.** By H. W. VOGEL (*Ber.*, 13, 1204—1208).—Collodion plates prepared with an excess of silver nitrate are more sensitive than those prepared with an excess of potassium bromide. Gelatin plates made with excess of silver nitrate are more sensitive than the others, but are excluded from use by faultiness. The sensitiveness of collodion plates may be increased by use of morphine, pyrogallol, &c. The latter increases the sensitiveness of gelatin plates somewhat, but morphine does not. Gelatin emulsion is made more sensitive by adding excess of ammonia, which is not the case with collodion emulsion, and silver bromide collodion emulsion in presence of certain chemicals can by addition of pigments be made more sensitive to certain coloured rays (*Ber.*, 9, 669). This is not the case with gelatin emulsions. Gelatin emulsions are made more sensitive by continued digestion, which is not the case with collodion. The author shows that these differences of behaviour of gelatin and collodion silver bromide emulsions may be explained by the properties of gelatin by the action of the different chemicals on it, and further by the different forms in which silver bromide is precipitated in gelatin emulsions and in collodion emulsions. In the former, it may be obtained in a more finely divided state, and consequently more sensitive to light.

P. P. B.

**Electric Conductivity of Carbon as affected by Temperature.** By W. SIEMENS (*Ann. Phys. Chem.* [2], 70, 560—574).—Matthiessen having stated that the electric conductivity of gas-retort carbon increases with the temperature, whilst Beetz found no such increase with artificial coke, and Auerbach has asserted (1879) that the resistance of gas-retort coke, like that of metals, increases with the temperature, the author has investigated the subject afresh. His experiments confirm Matthiessen's statement as to gas-retort coke, and they show that artificial coke also follows the same law. He traces the contradictory results of Beetz and of Auerbach to defective methods of connecting the pieces of coke with the circuit wires.  
R. R.

**Galvanic Polarisation.** By W. BEETZ (*Ann. Phys. Chem.* [2], 70, 348—371).—The views of polarisation entertained by several physicists, and particularly by Exner, are discussed in this paper. The



author explains the methods of measurement used by him in a series of experiments, the results of which lead to the conclusion that with a current of constant intensity and electromotive force, the polarisation of the two platinum electrodes is exactly alike, and the effect is the same whether the polarisation be caused by oxygen or by hydrogen.

R. R.

**Direct Transformation of Radiant Heat into Electricity.** By W. HANKEL (*Ann. Phys. Chem.*, **70**, 618—631).—The paper describes in detail the effects of radiant heat on a crystal of quartz in producing electric phenomena distinct from the ordinary pyroelectric manifestations hitherto recognised, although in some way related to them. The heat rays were made to traverse the crystal in the direction of the secondary axes, and the edges at which the rays entered, and also the opposite edges, were found to give indications of changes of positive or of negative electricity according to the crystallographic relations of the axes. The phenomena are discussed in connection with the author's circular-undulation theory of electricity.

R. R.

**An Aluminium Battery.** By F. WÖHLER (*Liebigs Annalen*, **204**, 119—120).—Under certain conditions aluminium immersed in strong nitric acid gives a tolerably strong current when brought into contact with another piece of the same metal.

A glass vessel 4 to 6 inches high is filled with very dilute hydrochloric acid or caustic soda; an inner porous vessel contains concentrated nitric acid. In each vessel is placed a cylinder of aluminium provided with a projecting piece passing through holes in the cover. To the projecting pieces are fastened short thick copper wires, between which is stretched a thin piece of platinum wire. As soon as the cylinders come in contact with the liquids, the platinum becomes white hot.

G. T. A.

**Molecular Heats and Molecular Volumes of the rare Earths and their Salts.** By L. F. NILSON and O. PETTERSSON (*Der.*, **13**, 1459—1465).—The specific weight and the specific heat of the following oxides and salts were determined:—

|                               | Specific weight. | Specific heat. | Molecular heat. | Molecular volume. |
|-------------------------------|------------------|----------------|-----------------|-------------------|
| $\text{Be}_2\text{O}_3$ ..... | 3·016            | 0·2471         | 18·61           | 24·97             |
| $\text{Al}_2\text{O}_3$ ..... | 3·990            | 0·1827         | 18·78           | 25·76             |
| $\text{Sc}_2\text{O}_3$ ..... | 3·864            | 0·1580         | 20·81           | 35·19             |
| $\text{Ga}_2\text{O}_3$ ..... | —                | 0·1062         | 19·54           | —                 |
| $\text{Yb}_2\text{O}_3$ ..... | 5·046            | 0·1026         | 23·29           | 44·99             |
| $\text{In}_2\text{O}_3$ ..... | 7·179            | 0·0807         | 22·17           | 38·28             |
| $\text{Er}_2\text{O}_3$ ..... | 8·640            | 0·0650         | 24·70           | 43·98             |
| $\text{Yb}_2\text{O}_3$ ..... | 9·175            | 0·0646         | 25·45           | 42·94             |
| $\text{La}_2\text{O}_3$ ..... | 6·480            | 0·0749         | 24·42           | 50·81             |
| $\text{D}_2\text{O}_3$ .....  | 6·950            | 0·0810         | 27·62           | 49·47             |
| $\text{ZrO}_2$ .....          | 5·850            | 0·1076         | 19·13           | 20·86             |

|  | Specific weight. | Specific heat. | Molecular heat. | Molecular volume. |
|--|------------------|----------------|-----------------|-------------------|
| CeO <sub>2</sub> .....   | 6·789            | 0·0877         | 15·04           | 25·45             |
| ThO <sub>2</sub> .....   | 9·861            | 0·0548         | 14·47           | 26·77             |
| Be <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 2·443            | 0·1978         | 62·37           | 129·07            |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 2·710            | 0·1855         | 63·59           | 126·50            |
| Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 2·579            | 0·1639         | 62·42           | 145·80            |
| Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·012            | 0·1718         | 67·41           | 130·27            |
| Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·097            | 0·1656         | 66·24           | 129·16            |
| Ga <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | —                | 0·1460         | 61·90           | —                 |
| Y <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                       | 2·612            | 0·1319         | 61·60           | 178·80            |
| In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·438            | 0·1290         | 66·41           | 149·77            |
| La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·600            | 0·1182         | 66·90           | 157·22            |
| Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·912            | 0·1168         | 66·23           | 144·94            |
| Di <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·735            | 0·1187         | 68·96           | 155·55            |
| Er <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·678            | 0·1040         | 64·48           | 168·57            |
| Yb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | 3·798            | 0·1089         | 65·87           | 167·15            |
| Tb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....                      | —                | 0·0972         | 41·21           | —                 |
| Be <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 12H <sub>2</sub> O ..... | 1·713            | —              | —               | 310·17            |
| Y <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O .....   | 2·540            | 0·2257         | 137·91          | 240·55            |
| La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 9H <sub>2</sub> O .....  | 2·853            | 0·2083         | 151·64          | 255·17            |
| Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 5H <sub>2</sub> O .....  | 3·220            | 0·1999         | 131·33          | 204·04            |
| Di <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O .....  | 2·878            | 0·1948         | 141·23          | 251·91            |
| Er <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O .....  | 3·180            | 0·1808         | 138·13          | 240·25            |
| Yb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O .....  | 3·286            | 0·1788         | 139·11          | 236·79            |

From these numbers, it is seen that in a group of isomorphous compounds the molecular heat increases, whilst the molecular volume diminishes with the increasing atomic weights of the metals.

The magnetic properties of the oxides were examined by Ångström:—

Magnetic .... Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Di<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>.

Diamagnetic.. Be<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub>.

W. C. W.

**Heat of Formation of Hydrocyanic Acid and Cyanides.** By BERTHELOT (*Compt. rend.*, 91, 79—83).—Two reactions were made use of in order to determine the heat of formation of hydrocyanic acid; firstly, its transformation into formic acid and ammonia; secondly, the conversion of cyanogen chloride into carbonic anhydride, hydrochloric acid, and ammonia. The heat of formation of ammonia which is involved in these calculations was taken at +35·15 units as determined by Thomsen; Berthelot has, however, shown that this number must be reduced to +21·0; consequently the number originally obtained for hydrocyanic acid must be reduced by 14·15. By the first method, the heat absorbed, —8·4 units, becomes therefore —22·55 units for the liquid acid, and —28·25 for the same in the gaseous state. The second method gave —10·1 units; this will now be —24·25 and —30·0 units respectively. As very many data are required in these calculations, it was thought advisable to eliminate altogether the heat of formation of ammonia, and to measure the

results, if possible, in a direct manner by exploding the gaseous acid with oxygen.

For this purpose, 0.14 gram of the pure liquid acid was enclosed in a thin glass bulb, and introduced into the steel calorimetric bomb described in a previous communication. The bomb having been filled with oxygen was closed, and the bulb broken. The acid volatilised rapidly at 18°, and the explosion was effected without difficulty. The carbonic anhydride produced was subsequently pumped out of the apparatus, and received in weighed potash bulbs, whereby a valuable control was obtained over the accuracy of the combustion; in this way it was found that a trace of hydrocyanic acid, about one-hundredth part, always escaped combustion; this was determined for every experiment in the potash after the latter had been weighed, and allowed for in the succeeding calculations. The numbers obtained at constant volume have been corrected to constant pressure.

One molecule of hydrocyanic acid in grams gave, from the initial weight of acid, 158.4 units; from the carbonic anhydride produced, 160.2; mean, 159.3 units. This number exceeds the heats of combustion of the carbon and hydrogen contained in the acid:—

$$\begin{array}{rcl} \text{C (diamond)} + \text{O}_2 \dots & = & + 94.0 \\ \text{H}_2 + \text{O} = \text{H}_2\text{O liquid} & = & + 34.5 \\ \hline & & 128.5 \end{array}$$

So that the formation of hydrocyanic acid from its elements gives  $+128 - 159.3 = -30.2$  units, a number which is practically concordant with those obtained by the indirect methods; the mean of the whole is  $-29.5$  units. A complete table accompanies this communication, showing the heat disengaged in the formation of a large number of the haloid and metallic combinations of cyanogen.

J. W.

**Thermochemical Research on Cyanogen and Hydrocyanic Acid.** By J. THOMSEN (*Ber.*, 13, 1392—1394). The heat of formation of gaseous hydrocyanic acid, as deduced by Berthelot from the heat evolved in the decomposition of hydrocyanic acid by strong hydrochloric acid, is incorrect. Instead of  $-9740$  the true value is  $-28360$ . The results based on the former number are consequently incorrect. The corrected values are—

|   | Heat of<br>combustion.  | Heat of<br>formation. |
|---|-------------------------|-----------------------|
| $\text{C}_2\text{N}_2$ .....              | 261290                  | $-67370$              |
| $\text{CNH}$ .....                        | 159500                  | $-28360$              |
| $\text{N} + \text{H}_3$ .....             | —                       | 11340                 |
| $\text{C}_2\text{N}_2 + \text{H}_2$ ..... | —                       | 10650                 |
| $\text{N} + \text{C} + \text{H} \dots$    | } for gaseous<br>carbon | 10540                 |
| $\text{C}_2 + \text{N}_2$ .....           |                         | 10430                 |

W. C. W.

**Constitution of Isomeric Hydrocarbons.** By J. THOMSEN (*Ber.*, 13, 1388—1391).—The heat of formation of a hydrocarbon can be calculated from the following formula:— $(\text{C}_n\text{H}_{2m}) = -nd + 2mq$

+  $xv' + yv'' + zv'''$ , when  $d$  = the heat of dissociation of carbon;  $2q$  = the heat developed by the combination of an atom of carbon with a molecule of hydrogen, and  $x$ ,  $y$ , and  $z$  are the number of single, double, and triple linkings.

Since the values of  $g$ ,  $v'$  and  $v''$  are nearly equal, they may be represented by  $r = 14570$ ; and  $v'''$  is so small that it may be neglected, the following simplified formula may be used:  $(C_n H_{2m}) = -n.38900 + (2m + x + y) 14570$ ,  $d$  being equal to  $38900^\circ$ .

The constitution of isomeric hydrocarbons may in many instances be ascertained from their heat of formation, since a double linking of two carbon atoms has a considerable influence on this value, *e.g.*, the heat of formation of propylene was found to be  $-400$ , which shows that its constitution is  $\text{H}_2\text{C}:\text{CH}.\text{CH}_3$ , and not  $\text{H}_3\text{C}.\text{C}.\text{CH}_3$ , since the calculated heat of the former compound is  $-150^\circ$ , and that of the latter  $+14430^\circ$ .

W. C. W.

**Variations in the Coefficient of Expansion of Glass.** By J. M. CRAFTS (*Compt. rend.*, 91, 413—415).—Since the coefficient of glass varies with the temperature, it is clear that the interval between any two points on a thermometer varies and the graduation becomes incorrect. By heating a thermometer for some time to 335°, and then cooling it slowly, the coefficient of expansion is diminished, so that if the zero point be raised  $t^{\circ}$ , then 100° is raised  $100 + t + t'$ .

By determining the coefficient of expansion of glass between 0° and 100° and 0° and 216.14° before and after heating to 335°, it is found that—

|  |                   |
|--|-------------------|
| Between 0° and 100° before heating to 335° | $k = 0.00002784$  |
| "      "      after      "      "          | $k = 0.000027405$ |
| 0° and 216.14° before      "      "        | $k = 0.00002979$  |
| "      "      after      "      "          | $k = 0.00002914$  |

which would have increased about 0.28 the value of  $100^\circ$  on the scale.

From a number of observations made on ordinary French glass, the value of  $k$  for different temperatures may be calculated from the formula  $k_t = a + bt + ct^2$ . It remains to be shown whether this formula remains constant for the same kind of glass after long heating and slow cooling, and also what effect the different degrees of tension produced by blowing the bulb has on the coefficient of expansion.

The author advocates the use of thermometers with limited scales (such as from  $200^{\circ}$  to  $300^{\circ}$ ) for high temperatures, instead of those registering from  $0^{\circ}$  upwards. L. T. O'S.

**Meyer's Method of Determining Vapour-densities.** By O. PETTERSSON and G. EKSTRAND (*Ber.*, 13, 1185—1191).—The authors have submitted this method to a comparison with that of Dumas, determining the vapour-densities of pure benzene, formic and acetic acids in steam, and in the vapours of toluene, turpentine, aniline, and nitrobenzene.

From this examination, it is found that Meyer's method gives results smaller than those obtained by Dumas, and further, there is less

concordance amongst the results with the former method than with the latter.

The authors point out the following sources of error in Meyer's method :—

(1.) The condensation of air on the surface of the vessel containing the substance. To neutralise this, experiments were made with formic acid sealed in a bulb, which was fastened on to a long glass rod passing through the caoutchouc stopper. The whole was then heated by the vapour of liquid used, and when it attained a constant temperature the bulb was broken by moving the glass rod. Still with this the vapour-density was found to be lower than by Dumas' method.

(2.) The chief error is the condensation of air on the substance itself; this error cannot be corrected, and its influence will vary with different bodies. The cause of the difference between the results of the two methods, in the case of formic and acetic acids and of benzene, is due to the presence of air or nitrogen, for Playfair's and Naumann's investigations have shown that in the presence of a permanent gas the vapour-densities of these bodies approach the normal. The authors show also that the influence of the condensed air is great in case of solids at 220°, and must be still more so at higher temperatures.

P. P. B.

**Critical Point of Mixed Vapours.** By J. DEWAR (*Chem. News*, 42, 15—17).—*Carbonic Anhydride and Carbon Bisulphide*.—Carbonic anhydride at 19° liquefies in presence of carbon bisulphide under a pressure of 49 atmospheres, and the liquid floats on the surface of the bisulphide. The same phenomenon was observed at—

|     |                  |                |   |
|-----|------------------|----------------|---|
| 35° | at a pressure of | 78 atmospheres |   |
| 40  | „ „              | 85             | „ |
| 58  | „ „              | 110            | „ |

At 47°, and a pressure of 80 atmospheres, the layers of liquids were not so definitely marked. On increasing the pressure to 110 atmospheres, the upper layer of liquid almost entirely disappeared, and on reducing the pressure to 80 atmospheres, the liquids mixed completely; a further reduction of 5 atmospheres caused them to separate. On quickly reducing the pressure to 58 atmospheres, and gradually increasing it to 85 atmospheres, the liquids again mixed.

*Carbonic Anhydride and Chloroform*.—At 18° and a pressure of 25 atmospheres, carbonic anhydride liquefies, forming a layer on the surface of the chloroform. On increasing the pressure to 50 atmospheres, the two liquids mixed completely after standing for a few minutes. At 33° the liquid forms under a pressure of 35 atmospheres, and at a pressure of 55 atmospheres the two liquids mix. At 55° the liquid forms at a pressure of 50 atmospheres, and at 67° under a pressure of 85 atmospheres, the two liquids in each case dissolving each other after standing for a few minutes.

*Carbonic Anhydride and Benzene*.—In presence of benzene, carbonic anhydride at 18° begins to liquefy under a pressure of 25 atmospheres, and dissolves in the benzene, the solution becoming saturated, any further quantity of condensed liquid floating on the surface; but on

allowing the two liquids to stand for about five minutes, they mix completely. At 35°, the gas liquefies under a pressure of 35 atmospheres. At this temperature, liquid carbonic anhydride is only sparingly soluble in benzene. At 52° the liquid formed under a pressure of 60 atmospheres, and at 70° under 85 atmospheres.

*Carbonic Anhydride and Ether.*—At 20° a pressure of 20 atmospheres is required to liquefy carbonic anhydride in presence of ether. The two liquids mix in all proportions. At 42° under a pressure of 55 atmospheres a distinct layer of carbonic anhydride is formed, and appears to slowly dissolve in the ether. A distinct layer of liquid at 68° is formed under a pressure of 110 atmospheres.

*Carbonic Anhydride and Nitrous Oxide.*—These two gases when liquefied mix together in all proportions. On reducing the pressure, one liquid evaporates before the other, and a distinct line of separation appears for a short time.

*Carbonic Anhydride and Phosphorus Trichloride.*—At 16·2° and 42·95 atmospheres, the carbonic anhydride began to liquefy before the phosphorus trichloride, and when the latter appeared, a slight indistinct layer of carbonic anhydride floated on its surface, but the two liquids mixed together on standing for a few minutes. At 23°, and a pressure of 46·91 atmospheres, the same phenomenon was observed. At 30°, and under a pressure of 49·94 atmospheres, the carbonic anhydride began to liquefy; it is not so soluble in phosphorus trichloride at this temperature as at lower temperatures.

At 33° carbonic anhydride liquefies under 50·84 atmospheres

|    |   |   |       |   |
|----|---|---|-------|---|
| 40 | " | " | 56·88 | " |
| 50 | " | " | 66·53 | " |

With smaller quantities of substances the following results were obtained:—

|                |              |              |              |
|----------------|--------------|--------------|--------------|
| At 10·5° ..... | 22·70 atmos. | At 40° ..... | 36·36 atmos. |
| 16·5 .....     | 24·70 "      | 50 .....     | 49·67 "      |
| 22·8 .....     | 32·18 "      | 70 .....     | 76·61 "      |
| 30·0 .....     | 33·88 "      |              |              |

*Carbonic Anhydride and Carbon Tetrachloride.*—At 12·8° the carbonic anhydride begins to liquefy, forming a distinct layer on the surface of the chloride. The two liquids, however, dissolve each other after a short time. At 21·4°, 30°, 40°, 52°, and 58°, similar effects take place.\*

*Carbonic Anhydride and Methyl Chloride.*—Two volumes of carbonic anhydride and one volume of methyl chloride at 13·5° C. The methyl chloride liquefies first, and at a pressure of 26·67 atmospheres, the anhydride began to liquefy, and rapidly dissolves in the chloride at 20·05°. Liquid carbonic anhydride appears at 28·57 atmospheres.

*Carbonic Anhydride and Acetylene.*—Equal volumes of the two gases were condensed together, in which proportion they mix completely at the following temperatures:—

\* No details of the pressures required are given in this case.

|   |   |   |         |
|---|---|---|---------|
| At 13.5° the pressure was 25.23 atmospheres |   |   |         |
| 21.0  | " | " | 26.8 "  |
| 26.8  | " | " | 34.1 "  |
| 31.9  | " | " | 42.26 " |
| 39.0  | " | " | 55.3 "  |
| 41.0  | " | " | 75.52 " |

The last temperature is the critical point.

*Carbonic Anhydride and Hydrochloric Acid.*—The following are the temperatures and pressures at which a mixture of equal volumes of the two gases liquefy:—

|               |           |                |           |
|---------------|-----------|----------------|-----------|
| At 0.0° ..... | 36 atmos. | At 18.5° ..... | 59 atmos. |
| 5.0 .....     | 39 "      | 34.0 .....     | 83 "      |
| 8.0 .....     | 43.8 "    | 35.5 .....     | 90 "      |
| 10.1 .....    | 48.2 "    |                |           |

*Carbonic Anhydride and Bromine.*—At 40° and a pressure of 60 atmospheres, two distinct layers of bromine and liquid carbonic anhydride containing some bromine dissolved in it, appear; at 90 atmospheres' pressure, the two liquids are miscible.

*Carbonic Anhydride and Camphor.*—The camphor was melted, and allowed to adhere to the sides of the tube. At 12°, the camphor melts, and on increasing the pressure, two distinct layers are formed, the lower liquid being cloudy from dissolved camphor, the upper one quite clear. The two layers are always present at all temperatures up to 55°. The upper layer, however, diminishes with increase of temperature. At 40°, a thin layer remains even at a pressure of 125 atmospheres. A further experiment gave the following results. At 15° the camphor melts at a pressure of 27.7 atmospheres; by increasing the pressure to 37 atmospheres, two distinct layers of liquid are formed, which become homogeneous after a short time. At 35°, two layers are formed under a pressure of 80 atmospheres. At 100 atmospheres, the two liquids mix. At 45°, the same takes place under 100 atmospheres, and the two liquids disappear on increasing the pressure. At 42.5°, the pressure being suddenly reduced, the camphor crystallises, and on increasing the pressure to 27.6 atmospheres, the camphor liquefies completely without further increase of pressure. At 60°, the lower layer of liquid remained at a pressure of 100° atmospheres.

*Carbonic Anhydride, Air, and Camphor.*—A mixture of 4 volumes carbonic anhydride and 1 volume air, was saturated with camphor-vapour. On increasing the pressure at 25°, the camphor liquefied; at 50°, a quantity of liquid formed under a pressure of 65 atmospheres; on increasing the temperature to 60°, the pressure remaining the same, crystals of camphor separated out on the tube above the liquid; they disappeared on increasing the pressure to 70 atmospheres. At 65°, on reducing the pressure from 70 to 65 atmospheres, camphor crystals again separate out, and redissolve on increasing the pressure to 73 atmospheres. On decreasing the temperature to 15°, camphor separated out from the liquid, and dissolved again on increasing the pressure, although it could not be separated again by reducing the

pressure. These effects may be due to supersaturation, and the effect of pressure on adding solubility when contraction takes place during solution.

It appears from the above experiments that carbonic anhydride in presence of various substances acts at high pressures as though it produced unstable compounds, which are decomposed and reproduced according to the conditions of temperature and pressure of the medium.

L. T. O'S.

**Lowering of the Freezing Point of Water by Pressure.** By J. DEWAR (*Chem. News*, 42, 1—2).—To test the accuracy of the pressure gauge of Cailletet's pump and the constancy of thermal junctions under pressure, experiments were made on the influence of pressure on the freezing point of water.

In the experiments, a movement of the galvanometer to the negative side showed a cooling effect of the junction inside the bottle. Two thermal junctions were used, consisting of iron-copper wire insulated by marine glue, the junction being covered with a thin layer of gutta-percha. One junction was placed inside the bottle to show the influence of pressure under different circumstances, the other was kept outside at zero.

*Series I.*—One junction was fixed in a brass flange frozen in a test-tube containing boiled water placed in an iron bottle and surrounded with water at  $0^{\circ}$ ; the bottle was also packed with ice. The pressure was raised in different experiments from 300 to 700 atmospheres in steps of 25 atmospheres at a time. The mean deflection obtained for 25 atmospheres was 19.7 on the scale (1 division =  $\frac{1}{1\frac{1}{2}}^{\circ}$  C.) or  $0.18^{\circ}$  C., which gives a reduction of  $0.00027^{\circ}$  for 1 atmosphere pressure.

*Series II.*—The junction was placed in a quill open at both ends and surrounded with water at  $0^{\circ}$ ; the iron bottle was packed as in Series I. The total deflection obtained for 200 atmospheres was 4 divisions =  $\frac{1}{3}^{\circ}$  C. This result is in accordance with Joule's experiments on the compression of water.

*Series III.*—The junction was surrounded with a mixture of water and ice and the iron bottle packed as before. In this case similar results were obtained to those in Series I, a mean deflection of 19.4 divisions for every 25 atmospheres.

*Series IV.*—In these experiments, the junction was surrounded with brine and placed in the bottle, which was packed with ice and salt to reduce the temperature to  $-20^{\circ}$ . The junction outside was also placed in ice and salt. A heating effect was produced which decreased as the pressure increased, the total increase in temperature being  $\frac{1}{15}^{\circ}$  C. for 200 atmospheres' pressure.

*Series V.*—The junction, frozen in a block of ice, was placed in the bottle and surrounded with brine at  $-20^{\circ}$ ; the bottle was packed with ice and salt. A slight heating effect was produced,  $1\frac{1}{2}$  divisions of the scale for 200 atmospheres.

*Series VI.*—These experiments were similar to Series I, excepting that mercury instead of water surrounded the junction in the test-tube. The results obtained were exactly the same as those above mentioned,



but owing to the heating of the mercury by compression the experiments could not be continued for long, since the ice rapidly melted.

*Series VII.*—Since the junction appeared to be affected by continual subjection to pressure, and in some cases worked somewhat irregularly, both junctions, insulated by marine glue, were placed in the flange; one was frozen inside the test-tube and the other remained outside and placed in the bottle, and both subjected to pressure. Exactly the same results were obtained as when one junction was placed outside the bottle, but still after repeating the experiment two or three times irregularities occurred. To prevent the junction being subjected to pressure, an iron tube closed at the bottom, about a quarter of an inch internal diameter and long enough to reach to the centre of the bottle, was soldered into the flange; a few drops of alcohol were placed in the tube and the junction was lowered into it from outside, the portion of the tube in the bottle was frozen into a test-tube and thus sustained the pressure, any alteration in temperature being conveyed through the iron to the junction. In this case also the results corresponded with those previously obtained.

These results prove that those deduced from the observed differences of volume of ice and water and the latent heat of fluidity under one atmosphere pressure are correct. It may therefore be assumed that  $\frac{TV}{L} = \text{constant}$  where  $V$  is the difference of volume and  $L$  the latent heat of fluidity. If  $V$  is assumed to be approximately constant, then  $T \times L$  is the latent heat of ice diminished as the freezing point is diminished by pressure.

L. T. O'S.

**Oven for Heating Sealed Tubes.** By L. v. BABO (*Ber.*, 13, 1219—1223).—The author describes a new form of such oven possessing many advantages, and in which by the circulation in it of the heated gases from the source of heat an equable temperature is obtained. Further, an arrangement is described by which the amount of gas burnt is regulated so as to obtain a constant temperature. For details the original must be consulted.

P. P. B.

**Lecture Experiments.** By M. ROSENFELD (*Ber.*, 13, 1475—1477).—1. Change of temperature produced when salts dissolve.

2. Absorption of ammonia and hydrochloric acid by water.

3. Crystallisation of sulphur and of mercuric iodide from solution in acetic anhydride.

W. C. W.

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## Inorganic Chemistry.

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**Vapour-density of Iodine, &c.** By BERTHELOT (*Compt. rend.*, 91, 77—78).—This paper is merely a statement of the author's opinion that inasmuch as V. Meyer and others have shown that iodine and the other halogens at high temperatures and low pressures do not obey the laws of Mariotte and Gay-Lussac, as established upon three ele-

mentary gases only, and as the diminution of density in the case of iodine is moreover progressive, no correct conclusion can be drawn with respect to variation in the number of molecules. He thinks that one law only remains universally applicable to the elements, namely, the invariability of their relative combining weights, that is to say, the notion of equivalents.

J. W.

**Ozone.** By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, 91, 228—230).—The tension of the transformation of oxygen into ozone is dependent on both the temperature and pressure. This tension increases rapidly as the temperature decreases, being at  $-23^{\circ}$  nearly double what it is at  $20^{\circ}$ . For temperatures above  $0^{\circ}$ , the proportion of ozone produced is greatest when the pressure is above 0.5 atmosphere. By raising the temperature, the rate at which the ozone is formed is lessened, and it is also more difficult to complete the reaction, especially if the gas is rarefied; and it may be that this maximum is consequent on the slowness with which the transformation takes place.

The proportion of ozone to the total volume of gas is not influenced by pressures below certain limits (about 180 mm.). This transformation of oxygen under the influence of the electric spark is analogous to the dissociation of compound gases, which at certain temperatures is limited by tension proportional to the total pressure. In the case of hydriodic acid, the proportion of free iodine and hydrogen increases as the pressure diminishes, and in the case of the formation of ozone, the proportion of the oxygen in relation to the ozone also increases as the temperature diminishes.

L. T. O'S.

**Formation of Hydrogen Peroxide and Ozone.** By A. R. LEEDS (*Chem. News*, 42, 17—19).—The author proves that both hydrogen peroxide and ozone are formed by the action of air on moist phosphorus. On heating the ozonised air, the quantity of water formed by the decomposition of the hydrogen peroxide increases regularly, whilst that of the ozone decreases, until at a temperature of  $200^{\circ}$  both are completely decomposed.

That ozone and hydrogen peroxide in the dilute state can exist together without much loss is also proved, and it is shown that the proportion the two gases bear to one another is 3 to 1.

Oxygen from which all traces of ozone and hydrogen peroxide have been removed by strong heating oxidises an acid solution of potassium iodide, it is therefore necessary that the reagent used for the detection of ozone should be perfectly neutral.

L. T. O'S.

**Vapour-densities of Selenium and Tellurium.** By H. ST. CLAIRE DEVILLE and TROOST (*Compt. rend.*, 91, 83—85).—Recent experimental research having reopened questions respecting the vapour-densities of selenium and tellurium, it is thought advisable by the authors to give full details of their work in connection with this subject. The analyses were executed 20 years ago, and at the time of publication a summary only was given. For obvious reasons these details cannot be wholly reproduced in abstract.

In comparing at a very high temperature the vapours of iodine and selenium, the increase in weight of the flask in the case of selenium was 0.014 gram, in the case of iodine 0.011 gram. It was then remarked that "there is a manifest error in the weight of iodine remaining in the flask, for with the number 0.011 gram a temperature of nearly 2,000° would be attained;" to this is now added, "owing to the recent experiments of Victor Meyer, that which appeared erroneous in 1860 may now be considered as correct."

The vapour-density of selenium was also taken in a porcelain globe and compared with that of air contained and heated in a similar apparatus. The calculated temperature being 1,420°, the theoretical density became 5.54; the density actually found was 5.68.

Operating in a similar manner with tellurium, the results of its vapour-density determination were, at a temperature of 1,439°, theory 8.93, experiment 9.0; at a temperature of 1,390°, theory 8.93, experiment 9.08. J. W.

**Ammonia in Air and Water.** By A. LÉVY (*Compt. rend.*, 91, 94—97).—*Rain Water.*—Although individual analyses of rain water collected from different quarters of Paris show varying proportions of ammoniacal nitrogen, the mean monthly and yearly results are sensibly identical. The quantity of nitrogen decreases pretty regularly in passing from the cold to the warm season of the year, generally reaching its minimum in July; the mean result for that month in 1879 was 0.93 mgrm. per litre of water, and the mean for the year, with four recording stations, 1.17 mgrms.

In the latter months the drinking water of Paris also shows a minimum of ammoniacal nitrogen, 0.21 mgrm. per litre; the maximum 0.27 mgrm. occurring in December; the small difference between these numbers shows the great uniformity of the Paris water supply.

The yearly means in 1879—1880 were—

|            |            |              |              |
|------------|------------|--------------|--------------|
| Vaune..... | 0.21 mgrm. | Ourcq.....   | 0.22 mgrm.   |
| Dhuis..... | 0.24 „     | Seine.....   | 0.22 „       |
| Marne..... | 0.24 „     | (Sewage).... | 20.00 mgrms. |

Summing up the results of four years analyses of rain water collected at the Observatory of Montsouris we have—

| September<br>to August. | Rain gauge. | Mean<br>per litre. | Nitrogen per<br>square metre. |
|-------------------------|-------------|--------------------|-------------------------------|
| 1875—1876               | 541.5 mm.   | 1.98 mgrm.         | 1074.78 mgrm.                 |
| 1876—1877               | 601.7 „     | 1.54 „             | 929.65 „                      |
| 1877—1878               | 600.1 „     | 1.91 „             | 1149.40 „                     |
| 1878—1879               | 655.3 „     | 1.20 „             | 787.32 „                      |

*Air.*—Contrary to what has been observed in the case of rain water, ammonia was most abundant in the air during the hot season. Thus in 1878—1879 the total weight in winter corresponding to 153 days' analyses was 257.6 mgrms., giving as a mean 1.68 mgrms. per 100 cm.; in summer the total weight was 269.7 mgrms. for 129 days, or 2.09 mgrms. for 100 cm.

The same volume of air collected in the Paris sewers gave from 4.6 to 9.4 mgrms. of ammoniacal nitrogen.

These numbers differ from those obtained by Gräber, Kemp, and Fresenius, but accord very well with those of Ville and Schloësing.

J. W.

**Chemical Composition of certain Hydrated Oxides.** By J. M. v. BEMMELN (*Ber.*, 13, 1466—1469).—An examination of the hydrated oxides of silicon, manganese, and tin, shows that the composition of these bodies varies with the molecular condition of the oxide, and also with the temperature and the amount of moisture in the atmosphere. The hydrates have a definite dissociations-tension, which varies with the temperature and humidity of the atmosphere.

W. C. W.

**Isomeric Modification of Aluminium Hydrate.** By D. TOMMASI (*Compt. rend.*, 91, 231).—By allowing ordinary aluminium hydrate, precipitated by ammonia from a solution of alum, to stand with water for about three months, it undergoes a molecular change. It is only very sparingly soluble in acids and alkalis. In acetic acid it is insoluble. It has the same formula as the normal hydrate, but it does not combine with aluminium chloride to form an oxychloride. The author proposes to call it aluminium hydrate  $\delta$  to distinguish it from the normal hydrate  $\alpha$ , gibbsite  $\beta$ , and the colloïd hydrate of Graham,  $\gamma$ .

L. T. O'S.

**Potassium and Sodium Aluminates.** By A. B. PRESCOTT (*Chem. News*, 42, 29).—*Potassium Aluminate*.—On treating a decinormal solution and a deci- $1\frac{1}{2}$ -normal solution of potassium alum respectively with normal and decinormal solutions of caustic potash until the precipitate formed was just dissolved, it was found that in every case the proportion of potassium to aluminium in the soluble aluminate is represented by the formula  $K_2Al_2O_4$ , or  $Al_2 \left\{ \begin{matrix} O_2 \\ (KO)_2 \end{matrix} \right.$ , the equation being  $K_2Al_2(SO_4)_4 + 8KHO = K_2Al_2O_4 + 4K_2SO_4 + 4H_2O$ .

The quantity of potassium sulphate solution present for one part of soluble potassium aluminate in the different degrees of dilution is as follows:—

|  |                    |
|--|--------------------|
| With $Al_2$ deci- $1\frac{1}{2}$ -normal and K normal . . . .    | 79 parts solution. |
| „ $Al_2$ decinormal and K normal . . . . .                       | 91 „               |
| „ $Al_2$ deci- $1\frac{1}{2}$ -normal and K decinormal . . . . . | 445 „              |
| „ $Al_2$ decinormal and K decinormal . . . . .                   | 456 „              |

The same compound is obtained by saturating caustic potash with aluminium hydrate, evaporating to dryness, and extracting the excess of alkali by alcohol (*Pogg. Ann.*, 7, 723).

Frémy (*Ann. Chim. Phys.* [3], 12, 362; *Compt. rend.*, 15, 1106) obtained it in a crystalline form by fusing the residue; he also states that  $K_2Al_2O_4$  is decomposed by much water, aluminium hydrate being precipitated, and  $Al_2(KO)_4$  is probably left in solution.

*Sodium Aluminate*.—Similar experiments were made with alum and caustic soda with similar results, the formula for the compound being

$\text{Al}_2 \left\{ \begin{smallmatrix} \text{O}_2 \\ (\text{NaO})_2 \end{smallmatrix} \right.$ , formed according to the equation  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 + 8\text{NaHO} = \text{Na}_2\text{Al}_2\text{O}_4 + \text{K}_2\text{SO}_4 + 3\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$ . The greatest dilution was 1 part of aluminate in 546 parts solution, and the least 1 part in 95 parts. Tissier (*Compt. rend.*, 48, 627, and *Jahr. Chem.*, 1859, 143) obtained four different compounds,  $\text{Na}_2\text{Al}_2\text{O}_4$ ,  $\text{Na}_6\text{Al}_2\text{O}_6$ ,  $\text{Na}_4\text{Al}_2\text{O}_6$ , and  $\text{Na}_8\text{Al}_2\text{O}_8$ .  
L. T. O'S.

**Atomic Weight of Glucinum.** By L. F. NILSON and O. PETERSSON (*Ber.*, 13, 1451—1459).—The authors have determined the atomic weight of glucinum by the analysis of the sulphate, and obtain the value 13.65 as the mean of four experiments. The specific heat of the metal increases with the temperature. Between  $0^\circ$  and  $100^\circ$ , specific heat = 0.4246, atomic heat = 5.79. Between  $0^\circ$  and  $300^\circ$ , specific heat = 0.5060, and the atomic heat = 6.90.

In reply to L. Meyer's statement (*Ber.*, 6, 576) that the atomic heat of oxygen calculated from the molecular heat of glucina,  $\text{G}_2\text{O}_3$ , is too low, viz., 2.47, the authors point out that this number closely agrees with that deduced from the specific heats of the other metals of this group,

|                               | At. heat of O. |                               | At. heat of O. |
|-------------------------------|----------------|-------------------------------|----------------|
| $\text{G}_2\text{O}_3$ .....  | 2.34           | $\text{Ga}_2\text{O}_3$ ..... | 2.88           |
| $\text{Al}_2\text{O}_3$ ..... | 2.35           | $\text{In}_2\text{O}_3$ ..... | 3.08           |
| $\text{Sc}_2\text{O}_3$ ..... | 2.67           |                               | W. C. W.       |

**Atomic Weight and Characteristic Salts of Scandium.** By L. F. NILSON (*Compt. rend.*, 91, 118—121, and *Ber.*, 13, 1439—1450).—The scandia used in these experiments was principally extracted from euxenite, but some residues from gadolinite and keilhauite were also at the disposal of the author.

The new earth may be separated from ytterbia by taking advantage of the fact that the nitrate decomposes more easily by heat than that of ytterbium, and that scandium sulphate produces in a saturated solution of potassium sulphate an insoluble double salt. This double salt nevertheless contains a little ytterbium sulphate, which may be finally removed by converting them into nitrates, and submitting the latter to partial decomposition by heat; the ytterbium nitrate can then be washed out.

The sample of scandia used for determining the atomic weight was prepared by dissolving the pure sulphate in water with addition of a little nitric acid, and precipitating it as oxalate; the oxalate when calcined yields scandia perfectly pure. A specimen prepared in this manner was examined spectroscopically by Thalén, who was unable to detect the presence of any foreign substance.

The atomic weight was found by weighing the oxide, converting it into sulphate, and weighing the sulphate produced. If the oxide be  $\text{Sc}_2\text{O}_3$ , then the mean of four experiments gives 44.03 as the atomic weight of scandium.

Scandia,  $\text{Sc}_2\text{O}_3$ , is a light, infusible, white powder resembling magnesia. It dissolves easily in boiling nitric and hydrochloric acids, but scarcely at all in the cold. It is not volatile, and gives no coloration

to flame, although a very brilliant spectrum may be obtained by the electric spark from the chloride.

The *nitrate* crystallises from a strong solution in small prisms; when strongly ignited, it is converted into oxide, but on treating this with water, a very basic nitrate generally dissolves, forming an opaque milky solution, which never becomes clear; this reaction is very characteristic of scandium.

The *sulphate*,  $\text{Sc}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$ , may be prepared as before mentioned; it is unalterable in the air, but loses 4 mols. of water at  $100^\circ$ , and the anhydrous salt is produced on gentle ignition; when strongly heated, it loses sulphuric acid and forms scandia.

The *double sulphate*,  $\text{K}_2\text{SO}_4 \cdot \text{Sc}_2(\text{SO}_4)_3 + x\text{H}_2\text{O}$ , forms small prisms grouped in a peculiar manner, which gives them a characteristic appearance. It is very slightly soluble in water, and quite insoluble in a saturated solution of potassium sulphate.

The *selenite* and *oxalate* may be made by precipitation with the corresponding sodium salts; both are insoluble.

The composition of the earth,  $\text{Sc}_2\text{O}_3$ , is proved by the following facts:—

1. Scandia is found in minerals associated with other rare earths of the formula  $\text{R}_2\text{O}_3$ .
2. Solutions of scandium and ytterbium salts behave in the same manner with oxalic acid.
3. There is great analogy between the behaviour of the nitrates of these two metals at high temperatures.
4. The composition of the double salt with potash shows that scandium belongs to the group of metals obtainable from gadolinite and cerite, all these metals giving salts of the same typical composition.
5. The insolubility of the same salt in a solution of potassium sulphate singles out scandium in particular as a member of the cerite group.
6. In the composition of the selenites, this earth presents great analogy on the one side to  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and on the other to  $\text{Al}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ , which furnish analogous acid salts.
7. The atomic weight, 44, is the number which Mendelejeff predicted for the undiscovered element *ekaboron*.
8. The specific heat and molecular volume of the earth and of the sulphates place scandia as intermediate between glucina and yttria.

J. W.

**Cerium Tungstate.** By A. COSSA and M. ZECCHINI (*Gazzetta*, 10, 225—232) —The cerium tungstate was prepared by gradually adding a solution of pure cerium sulphate to a cold aqueous solution of normal sodium tungstate, keeping the latter in slight excess; if the tungstate be added to the solution of cerium sulphate, the precipitate will be contaminated with the sparingly soluble sodium cerium sulphate. The yellowish flocculent precipitate dried at  $100^\circ$  has the composition  $\text{CeWO}_4 + \text{H}_2\text{O}$ , but loses its water on ignition, and fuses at a very high temperature, but more readily than scheelite. On cooling, it forms a sulphur-yellow crystalline mass, with conchoidal fracture; sp. gr. =  $6.514$  at  $12^\circ$ ; specific heat as determined by Naccari,  $0.0821$ .

That of scheelite is 0.1005 (Naccari) or 0.0967 (Kopp). Taking Ce as 92 this gives

|                         | Mol. weight. | Sp. heat. |                |
|-------------------------|--------------|-----------|----------------|
| CeWO <sub>4</sub> ..... | 340          | ×         | 0.0821 = 27.91 |
| CaWO <sub>4</sub> ..... | 288          | ×         | 0.1005 = 28.94 |
| CaWO <sub>4</sub> ..... | 288          | ×         | 0.0967 = 27.84 |

so that it would seem probable the cerium in cerium tungstate is bivalent like calcium. C. E. G.

**Zinc Oxide in Alkaline Solutions.** By A. B. PRESCOTT (*Chem. News*, 42, 30).—By treating a normal solution of zinc sulphate with a normal potash solution, it is found that at 17° C. 8 c.c. of the alkaline solution are required to redissolve the precipitate, and that 4 c.c. of a seminormal sulphuric acid solution can be added to the mixture before reprecipitation takes place. It therefore appears that the compound K<sub>2</sub>OZnO is formed according to the equation, ZnSO<sub>4</sub> + 4KOH = K<sub>2</sub>OZnO + K<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O. This compound has previously been obtained in the crystalline state by Laux (*Annalen*, 9, 165), and Frémy (*Compt. rend.*, 15, 1106). The solution with excess of alkali is reprecipitated by excess of water. Decinormal potash solution would not dissolve the precipitate. The weakest solution capable of dissolving the precipitate is  $\frac{16.5}{56.1}$   $\approx$  normal. At a temperature of 50°,

the solubility of the precipitate is greatly diminished.

Caustic soda forms a similar compound, Na<sub>2</sub>OZnO, which is more soluble in the alkali, requiring only an excess of 3 c.c.; at 50°, the solubility of the precipitate is also diminished.

Ammonia also forms a compound with zinc oxide. 1 c.c. of zinc sulphate requires 5 c.c. of normal ammonia solution, and the reaction takes place according to the equation 2ZnSO<sub>4</sub> + 10NH<sub>4</sub>HO = 3(NH<sub>4</sub>)<sub>2</sub>ZnO + 2(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 5H<sub>2</sub>O. The precipitate forms again on diluting the solution with water. Malaguti (*Compt. rend.*, 62, 413) obtained a crystalline zinc ammonium oxide having the composition NH<sub>3</sub>.ZnO.3H<sub>2</sub>O[NH<sub>4</sub>HO.Zn(OH)<sub>2</sub>.H<sub>2</sub>O], or Zn(OH)(NH<sub>3</sub>).3H<sub>2</sub>O. Weyl (*Jahresb.*, 1864, 165, and *Pogg. Ann.*, 123, 353) obtained the compound (NH<sub>3</sub>)<sub>2</sub>ZnO. The author considers the compound obtained

by himself to have the constitution

$$\left. \begin{array}{l} \text{ZnO} \\ \text{ZnO} \end{array} \right\} \begin{array}{l} \text{NH}_3 \\ \text{NH}_3 \\ \text{NH}_3 \\ \text{NH}_3 \\ \text{NH}_3 \\ \text{NH}_3 \end{array}$$

L. T. O'S.

**Silver-ammonium Oxide.** By A. B. PRESCOTT (*Chem. News*, 42, 31).—The compound formed when ammonia is added to silver nitrate in sufficient quantity to dissolve the precipitate first produced, may be represented by the formula,  $\left. \begin{array}{l} \text{NH}_3\text{Ag} \\ \text{NH}_3\text{Ag} \end{array} \right\} \text{O}$ , the reaction being



L. T. O'S.

**Two New Basic Copper Chromates. Non-existence of Potassium Copper Chromate.** By M. ROSENFELD (*Ber.*, 13, 1469—1475).—The precipitate which is formed when potassium chromate is added to a solution of copper sulphate, has the composition  $\text{CrO}_3 \cdot 3\text{CuO} + 2\text{H}_2\text{O}$ .

Although the colour of the substance varies with the temperature and concentration of the solutions, its composition is constant. The same salt is formed by digesting freshly precipitated copper hydroxide with a solution of potassium dichromate, but in this case it is mixed with crystals of potassium dichromate.

No change takes place when solutions of potassium dichromate and copper sulphate are mixed together, but if sufficient potash is added to convert the dichromate into neutral chromate, then  $\text{CrO}_3 \cdot 3\text{CuO} + 2\text{H}_2\text{O}$  is formed. If a larger quantity of potash is used, a yellow or a green precipitate will be thrown down. The former has the composition  $2\text{CrO}_3 \cdot 7\text{CuO} + 5\text{H}_2\text{O}$ , the green salt which changes to brown on drying has the formula  $\text{CrO}_3 \cdot 7\text{CuO} + 5\text{H}_2\text{O}$ . W. C. W.

**Fluorine Compounds of Uranium.** By A. DITTE (*Compt. rend.*, 91, 115—118).—When the green oxide of uranium,  $\text{U}_3\text{O}_8$ \*, is treated with hot concentrated hydrofluoric acid, it is rapidly attacked, with production of a yellow solution and an insoluble fine green powder. On evaporation the solution yields yellow transparent crystals which, when dried at  $120^\circ$ , have the formula  $\text{U}_2\text{F}_3 \cdot 4\text{HF}$ .

This fluohydrate, heated in a closed crucible, first melts, and then evolves fumes of hydrofluoric acid; if air has access, the fluoride is completely decomposed, and uranium protoxide is produced. The green substance before mentioned is insoluble in water, and very little soluble even on heating in dilute acids, other than sulphuric acid and aqua regia. It is an oxyfluoride to which analysis assigned the formula  $\text{U}_2\text{O}_3\text{F}$ .

The author regards the green oxide as capable of separating under favourable conditions according to the equation  $2\text{U}_3\text{O}_8 = 2\text{U}_2\text{O}_3 + \text{U}_2\text{O}_5$ ; in presence of hydrofluoric acid, the sesquioxide dissolves with formation of fluohydrate, whilst the protoxide behaving like an elementary body combines with the halogen of the acid, and liberates hydrogen. This reaction was verified by treating a known weight of the green oxide with hydrofluoric acid, and weighing the products of the reaction.

Uranyl fluoride,  $\text{U}_2\text{O}_3\text{F}$ , melts and decomposes at a bright red heat, giving off vapours which condense to yellowish-white transparent needles, and leaving behind brilliant black crystals of uranium protoxide. The reaction appears to be as follows:— $2\text{U}_2\text{O}_3\text{F} = \text{U}_2\text{OF}_2 + \text{U}_2\text{O}_3 + \text{O}$ .

The oxyfluoride,  $\text{U}_2\text{OF}_2$ , is very soluble in water; it melts and volatilises at a red heat, but in presence of air it is decomposed with formation of protoxide.

When uranyl fluoride is heated to redness in a current of hydrogen, it evolves hydrofluoric acid, and is ultimately converted into crystalline

\*  $\text{U} = 120$ .



protoxide; but as long as the reaction is incomplete and the salt retains fluorine, it yields a sublimate of oxyfluoride,  $U_2OF_2$ , if strongly heated in a close vessel. J. W.

**Chemistry of the Platinum Metals.** By T. WILM (*Ber.*, 13, 1198—1204).—According to v. Schneider (*Annalen*, Sup., 5, 261), pure palladium may be obtained from the filtrate of platinum-ammonium chloride, by precipitating the metals with zinc and dissolving out the copper and palladium by nitric acid. The palladium is then separated by treatment with mercury, whereby an amalgam is obtained, which on distillation leaves pure palladium. The author finds, however, that all the platinum metals when precipitated by zinc are soluble in nitric acid, also that it is not possible to remove palladium alone by shaking the solution with mercury, as the latter precipitates all platinum metals. A solution of platinum chloride may be decomposed by shaking with mercury, and a dark grey amalgam obtained. Further, the amalgam of platinum metals cannot be freed from mercury by distillation and ignition. By treating such an ignited residue with hydrochloric acid, and precipitation with ammonium chloride, a compound,  $PdCl_2 \cdot 5NH_4Cl \cdot Hg_2Cl_2$ , has been obtained; it crystallises in beautiful concentrically grouped needles; on ignition in hydrogen, it yields a residue of mercury and palladium. From the residue insoluble in hydrochloric acid, by dissolving in aqua regia and removing the platinum by ammonium chloride, a filtrate was obtained, which by treatment with salt, and ammonium chloride and alcohol, yielded palladium ammonium chloride. This the author finds has the composition  $PdCl_2 \cdot 2NH_4Cl$ , and does not contain water of crystallisation. On ignition it leaves a residue of spongy palladium, which exhibits the absorption of hydrogen in a very marked manner. P. P. B.

## Mineralogical Chemistry.

**Hemihedry of the Diamond.** By K. MARTIN (*Jahrb. f. Min.*, 1879, 156).—The author examined the fine collection of diamonds in the Leyden Museum, and found one specimen which in his opinion proved the hemihedry of the diamond. The crystal in question was apparently a fine triakisoctohedron 5 mm. in size, the faces being strongly striated and rounded off. Upon these faces the faces of the octohedron appeared to exist, but they exhibited alternately such a difference in size that the author concluded that the faces were those of the positive and negative tetrahedron, consequently the predominating form ("grundform") must be considered to be built up of the positive and negative deltoid-dodecahedron. The question to be answered was this: "Were the segments in the opposite lying octants of the octohedron dependent on each other in their growth?" It was evident that in the growth of each of the four segments (corresponding in position to a tetrahedron) there was a dependence. From this

the author concludes that, the crystal exhibited the following forms in combination:  $\frac{mO}{2} \cdot \frac{-mO}{2} \cdot \frac{O}{2} \cdot \frac{-O}{2}$ .

C. A. B.

**Two Regular Intergrowths of Different Minerals.** By A. SADEBECK (*Jahrb. f. Min.*, 1879, 154—155).—(1.) *Arsenical pyrites intergrown with Iron pyrites.*—Some fine crystals of arsenical pyrites from Freiberg were found to be covered by numerous crystals of iron pyrites. The arsenical pyrites exhibited the usual forms, the crystals being built up of numerous subindividuals in hypoparallel position, the axis parallel to which they arrange themselves being the vertical axis. The iron pyrites crystals are cubes characterised by the absence of the usual striation, the faces however appearing drusy, owing to the occurrence of numerous subindividuals also in hypoparallel position. These subindividuals do not exhibit sharply defined outlines, their faces and edges being more or less rounded or bent. The iron pyrites cubes occur in the arsenical pyrites crystals in such a manner that one of the crystallographical axes of the former coincides with the vertical axis of the latter, whilst the prismatic axes of both crystals also coincide. This peculiar law was first discovered by the author in the case of a similar intergrowth of iron pyrites with marcasite in some specimens of the last-named mineral from Tavistock. The occurrence of a similar intergrowth of the two isomorphous minerals (marcasite and arsenical pyrites) with iron pyrites, seems to show that the isomorphism is not due to form alone, but also to the molecular structure, as both minerals apparently exert an equal molecular attraction upon the iron-pyrites.

(2.) *Copper pyrites intergrown with Fahlerz.*—The author observed a very peculiar and interesting intergrowth of the above-mentioned minerals on some specimens from Kapnik, the crystallographical axis of the two minerals coinciding, so that the positive tetrahedron of the fahlerz lies in the same position as the negative tetrahedron (sphenoid) of the copper-pyrites, and *vice versa*. The edges of the two tetrahedrons intersect at right angles, so that the individuals occupy the same position as two regular tetrahedrons, twinned according to the law, "the twin-axis a prismatic axis." The copper pyrites tetrahedrons predominate, the combination being the positive tetrahedron (sphenoid) with modified solid angles, with occasionally the "first acuter" pyramid. The fahlerz crystals (exhibiting the combination positive tetrahedron, triakistetrahedron and rhombic dodecahedron) project from the faces of the copper pyrites tetrahedron. There is of course no real twin-formation in the above case, as the minerals are different and also the crystal-systems.

C. A. B.

**Microscopical Observations of the Growth and Resolution of the Alums in Solution of Isomorphous Substances.** By F. KLOCKE (*Jahrb. f. Min.*, 1879, 81—82).—There is nothing of importance in this paper to add to the author's previous observations (*Jahrb. f. Min.*, 1878, 958—959; this Journal, 36, 439).

C. A. B.

**Feuerblende (Rittingerite) from Chañarcillo.** By A. SCHRAUF (*Jahrb. f. Min.*, 1879, 144).—The author observes that the rittingerite of Joachimsthal described by him (*Sitzungsber. d. Wiener Akad.*, April 11th, 1872) seems to be identical with the mineral from Chañarcillo. The axial ratios are the same, and there is an analogous development of the forms. The following measurements will make this more apparent:—

Rittingerite . . . . . OP : P =  $48^{\circ} 52'$      $\infty P : \infty P = 124^{\circ} 20'$   
 Min. from Chañarcillo  $\infty P \infty : 5P5 = 48^{\circ} 56'$      $P \infty : P \infty = 124^{\circ} 37'$

The OP of Schrauf corresponds with the  $\infty P \infty$  of Streng. Schrauf states that the results of his examinations of true feuerblende agree with those of Miller. C. A. B.

**Manganese-Garnet.** By HEDDLE (*Jahrb. f. Min.*, 1879, 83).—Crystals of this garnet are found in various localities in Scotland, but particularly fine ones are found at Glen Skiag, in Ross, accompanied by muscovite crystals, tourmaline, and more rarely by zircon and apatite. The garnets are trapezohedrons, exhibiting two colours, the first being light red and often one inch in diameter, the second are brown and sometimes five inches in diameter. An analysis showed the two varieties to have the following composition, viz.:—

Light red garnet—

|                    |                                  |                                  |       |       |       |       |                   |
|--------------------|----------------------------------|----------------------------------|-------|-------|-------|-------|-------------------|
| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | FeO.  | MnO.  | CaO.  | MgO.  | H <sub>2</sub> O. |
| 35.99              | 16.221                           | 8.638                            | 23.27 | 15.24 | 0.408 | 0.471 | 0.249 = 100.482   |

Brown garnet—

|        |        |       |       |        |       |       |                 |
|--------|--------|-------|-------|--------|-------|-------|-----------------|
| 36.076 | 18.957 | 7.033 | 21.56 | 13.615 | 0.904 | 1.769 | 0.325 = 100.239 |
|--------|--------|-------|-------|--------|-------|-------|-----------------|

Similar garnets are at Struay Bridge and also at Ben Resipol, in Argyllshire. C. A. B.

**Desmine (Stillbite).** By A. v. LASAULX (*Jahrb. f. Min.*, 1879, 82, 83).—The author examined crystallographically and optically some desmine crystals from various localities, and concluded from the results obtained that desmine crystallises in the mono-symmetrical system, being isomorphous with harmotome and phillipsite. The axial relations were  $a : b : c = 0.70325 : 1 : 1.119395$   $P = \infty P$ ;  $\infty P \infty = OP$ ;  $OP = +P \infty$ ;  $\infty P \infty = \infty P \infty$ ;  $\infty P = P \infty$ . There are no simple crystals of desmine, but only twins, according to the same laws as those of harmotome and phillipsite. C. A. B.

**Analyses of Minerals and Rocks.** By A. HILGER (*Jahrb. f. Min.*, 1879, 127—132).—*Porphyry from the Paper Mill near Weilburg, Nassau.*—This rock was found to have a sp. gr. of 2.79 and the following composition, viz.:—

|                    |                                  |                                  |      |      |                    |                   |                   |                   |
|--------------------|----------------------------------|----------------------------------|------|------|--------------------|-------------------|-------------------|-------------------|
| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | CaO. | MgO. | Na <sub>2</sub> O. | K <sub>2</sub> O. | CO <sub>2</sub> . | H <sub>2</sub> O. |
| 61.12              | 16.96                            | 6.23                             | 1.13 | 0.85 | 4.37               | 4.63              | 2.78              | 1.36 = 99.33      |

There were traces also of manganese and sulphuric acid. The pre-

sence of carbonic anhydride is due to infiltration of calcium carbonate and ferrous carbonate, both of these substances being derived from the neighbouring rock. The manganese was present as manganoso-manganic oxide.

*Diorite from Diez in the Ruppachthal, Nassau.*—This rock is interpolated in great masses in the lower Devonian orthocerasic slates. An analysis was made of it with the following results, viz.:—

(a.) Soluble in hydrochloric acid—

| SiO <sub>2</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | Al <sub>2</sub> O <sub>3</sub> . | CaO. | P <sub>2</sub> O <sub>5</sub> . |                                  |
|--------------------|----------------------------------|----------------------------------|------|---------------------------------|----------------------------------|
| 0·84               | 6·83                             | 1·47                             | 2·69 | 0·001                           | = (with traces of alkalis) 11·83 |

(b.) Insoluble in hydrochloric acid—

| SiO <sub>2</sub> . | CaO. | Fe <sub>2</sub> O <sub>3</sub> . | Al <sub>2</sub> O <sub>3</sub> . | MgO. | Na <sub>2</sub> O. | K <sub>2</sub> O. |         |
|--------------------|------|----------------------------------|----------------------------------|------|--------------------|-------------------|---------|
| 6·44               | 0·51 | 4·90                             | 16·73                            | 0·7  | 3·00               | 0·85              | = 87·13 |

98·96

The amount of FeO was found to be 5·76 per cent., and that of the Fe<sub>2</sub>O<sub>3</sub> 4·23 per cent.

*Diallagite and Bronzite from Dun Mountain, near Nelson, New Zealand.*—Both these minerals occur intermixed in large foliated masses, penetrating olivine and serpentine.

*Bronzite.*—Sp. gr. = 2·58. Its chemical composition was found to be as follows, viz.:—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | CaO. | MgO.  | K <sub>2</sub> O. | Na <sub>2</sub> O. | FeO. | H <sub>2</sub> O. |         |
|--------------------|----------------------------------|------|-------|-------------------|--------------------|------|-------------------|---------|
| 41·82              | 6·28                             | 3·52 | 26·80 | 0·82              | 0·66               | 8·57 | 11·03             | = 99·50 |

There were traces also of Cr<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>.

*Diallagite.*—Sp. gr. = 3·19. Its chemical composition was found to be as follows, viz.:—

| SiO <sub>2</sub> . | CaO.  | MgO.  | Al <sub>2</sub> O <sub>3</sub> . | FeO. | H <sub>2</sub> O. |         |
|--------------------|-------|-------|----------------------------------|------|-------------------|---------|
| 52·23              | 20·15 | 16·85 | 4·71                             | 3·48 | 2·53              | = 99·95 |

The bronzite is much decomposed, notwithstanding its fresh appearance, whilst the diallagite is not so much decomposed.

*Pinitoid*, from Gleichlinger Fels in the Fichtelgebirge, occurs in light greyish-green masses in the decomposed granite, being a product of the decomposition of orthoclase. Sp. gr. 2·81; chemical composition as follows, viz.:—

| SiO <sub>2</sub> . | Al <sub>2</sub> O <sub>3</sub> . | CaO. | MgO. | K <sub>2</sub> O. | Na <sub>2</sub> O. | Fe <sub>2</sub> O <sub>3</sub> . | P <sub>2</sub> O <sub>5</sub> . | H <sub>2</sub> O. |         |
|--------------------|----------------------------------|------|------|-------------------|--------------------|----------------------------------|---------------------------------|-------------------|---------|
| 45                 | 29·96                            | 1·44 | 1·15 | 10·13             | 2·15               | 3·16                             | 0·32                            | 6·24              | = 99·79 |

*Zinc-blende* occurs in the keuper-sandstone (*Lettenkohlen sandstein*) of Rothenburg in foliated nodules. Its chemical composition was as follows, viz.:—

| Zn.   | S.    | Fe <sub>2</sub> O <sub>3</sub> . | Cu.    | Tl.    | Insoluble matter. |          |
|-------|-------|----------------------------------|--------|--------|-------------------|----------|
| 62·37 | 30·69 | 1·33                             | traces | traces | 5·64              | = 100·03 |

*Calamine* (Smithsonite) is found as a light-grey crust, accompanied

by iron pyrites and spathic iron and quartz at Ems, Nassau. Chemical composition as follows, viz.:—

| ZnO.  | CO <sub>2</sub> . | Fe <sub>2</sub> O <sub>3</sub> . | S.   | Insoluble matter. |
|-------|-------------------|----------------------------------|------|-------------------|
| 52.42 | 28.31             | 4.90                             | 1.30 | 12.17 = 99.10     |

The sulphur is combined with iron, forming 2.44 per cent. of iron-pyrites, the remaining iron being in the form of ferric oxide.

*Mixture of cinnabar, metacinnabarite, and stibnite*, from Huitzucs, in Mexico. Sp. gr. = 4.66. This mixture was analysed and found to have the following composition, viz.:—

| Hg.   | S.   | Sb.   | O.    | H <sub>2</sub> O. | Insoluble matter. |
|-------|------|-------|-------|-------------------|-------------------|
| 15.79 | 2.54 | 59.66 | 15.66 | 2.29              | 2.51 = 98.45      |

There is little doubt that the antimony really exists in the form of stibnite in this mixture, as the following shows, viz.:—

|                       |                   |              |   |
|-----------------------|-------------------|--------------|---|
| H <sub>2</sub> O .. = | 2.29 per cent. :  | 18 = 0.12 =  | 1 |
| Sb .... =             | 59.66     „     : | 122 = 0.49 = | 4 |
| O .... =              | 15.66     „     : | 16 = 0.97 =  | 8 |

Delfs (*J. pr. Chem.*, 40, 318), and Schnabel (*Pogg. Ann.*, 105, 146), found the formula of stibnite to be H<sub>2</sub>Sb<sub>2</sub>O<sub>3</sub> or Sb<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O. On igniting the mineral until the weight was constant, there was a loss of 22.15 per cent., a result which differs little from the percentage of mercury, sulphur, and water added together. The residue contained 59.24 per cent. of antimony.

*Pyromorphite from Dernbach, near Montabaur, Nassau.*—Crystals exhibiting the following forms in combination, viz.:—∞P, 0P, and P, were found imbedded in pyrolusite. On analysis their chemical composition was found to be as follows, viz.:—

| Pb.    | Ca.   | Cl.   | PO <sub>4</sub> . | Insoluble in nitric acid. |
|--------|-------|-------|-------------------|---------------------------|
| 75.070 | 0.300 | 2.133 | 21.267            | 0.313 = 99.083            |

Fluorine was not detected.

C. A. B.

**Heat of the Comstock Lode.** By J. A. CHURCH (*Chem. News*, 42, 42—43 and 52—53).—J. A. Phillips (*Quart. Jour. Geol. Soc.*, August, 1879) maintains that the heat evolved by the kaolinisation of the felspar rocks is not sufficient to raise the temperature of the Comstock Mine to 85°. In reply, the author upholds his theory, and points out that the amount of alkalis which enter into solution affords no measure of the quantity of rock which is undergoing the process, for there is a large amount of aqueous vapour which pervades the lode and enters into chemical combination with the kaolinised rock, evolving large quantities of heat without dissolving any of the alkalis, &c. There are moreover gaseous currents, the result of kaolinisation permeating the rocks, which carry the heat with them and distribute it throughout the whole mass.

G. F. Barker maintains that the heat is produced by the movement

of the rocks, but this movement is caused by the swelling of the rocks when their conditions have been altered artificially by excavation. There is no indication of any natural movement at a depth of 2,000 feet sufficient to produce the requisite amount of heat. The first thousand feet—although the principal zone of oxidation and solution—does not exhibit any unusual increase of temperature, the increase being about  $3.5^{\circ}$  for every hundred feet. L. T. Q'S.

**Two remarkable Meteors observed in Sweden.** By A. E. NORDENSKIÖLD (*Jahrb. f. Min.*, 1879, 77—81).—A meteor fell on the 18th of March, 1877, and was seen over the greater part of Sweden, exploding over Wernern Lake, which at the time was covered with ice. Some account of it is given by eye witnesses in *Verb. d. Geol. Ver. in Stockholm*, bd. 4, 73—75. Another meteor fell on the 28th of June, 1873, at Stalldalen in the middle of the day, whilst the sun was shining brilliantly. It was seen for a distance of about 450 kilometers. From the observations of several scientific men, the author is of opinion that the principal part of the cosmical substance of the meteorite consisted of a combustible substance, which left no residue behind, and the burning of this substance produced the brilliant light observed. The burning nucleus had a diameter of about 150 to 400 meters, and some observers were certain that the meteor consisted of two or more "fire-balls" following each other. It exploded at a height of about 38 kilometers, and 11 stones were collected, weighing in the aggregate about 35 kilograms. The ground-mass of the meteorite consists of a grey and a black shining substance, both containing numerous black shining faces, grains, and microscopical crystals of olivine disseminated throughout, also nickel-iron in grains and reticulated veins. The presence of magnetic iron pyrites was made apparent on a polished surface, whilst chondrodite was observed in thin sections, the resemblance of the meteorite to the Orvinio meteorite of Tschermak being very striking under the microscope. An analysis of the meteorite by Lindström showed it to have the following composition, viz. :—

|       | SiO <sub>2</sub>  | P <sub>2</sub> O <sub>5</sub> | Al <sub>2</sub> O <sub>3</sub> | A <sub>2</sub> O <sub>3</sub> | FeO   | MnO  | NiO  | CaO  | MgO     |
|-------|-------------------|-------------------------------|--------------------------------|-------------------------------|-------|------|------|------|---------|
| I ..  | 35.71             | 0.30                          | 2.11                           | 0.40                          | 10.29 | 0.25 | 0.20 | 1.61 | 23.16   |
| II .  | 38.32             | 0.31                          | 2.15                           | —                             | 9.75  | 1.00 | 0.42 | 1.84 | 25.01   |
|       | Na <sub>2</sub> O | K <sub>2</sub> O              | Fe                             | Ni                            | Co    | P    | S    | Cl   |         |
| I ..  | 0.62              | 0.15                          | 21.10                          | 1.61                          | 0.17  | 0.01 | 2.27 | 0.04 | =100.00 |
| II .. | Not determined    |                               | 17.48                          | 1.02                          | —     | —    | 2.51 | —    | = 99.81 |

The first gives the composition of the grey ground-mass, the second that of the black ground-mass; sp. gr. at  $23^{\circ}$  = 3.733. Nordenskiöld assigns the following constitution to the meteorite from Ställdalen, viz. :—

|                          | I.    | II.    |
|--------------------------|-------|--------|
| Magnetic iron pyrites .. | 5.74  | 6.36   |
| Nickel iron .....        | 19.42 | 14.65  |
| Soluble silicates .....  | 33.46 | 78.99  |
| Insoluble silicates..... | 40.69 |        |
| Chrome-iron .....        | 0.59  |        |
|                          | 99.90 | 100.00 |

The grey ground-mass becomes black on being heated either in the reducing or oxidising flame, and the author considers it probable that those stones which exhibit a grey colour have not been exposed to so high a temperature as the darker ones. Nordenskiöld recalculated the analyses of all the meteorites which most nearly approach the Stålldalen meteorite in chemical composition, and found (on expressing the constituents in the elementary form) that they were identical in composition, a fact which the following table will serve to illustrate, viz.:—

| Locality.                           | Analyst.                | Si.   | Mg.   | Fe.   | Ni.  | Co.   | Mn.   |
|-------------------------------------|-------------------------|-------|-------|-------|------|-------|-------|
| Erleben .....                       | Stromeyer ....          | 26.11 | 21.79 | 44.29 | 2.43 | —     | 0.83  |
| Lixna .....                         | A. Kuhlberg ..          | 26.70 | 23.61 | 42.90 | 2.68 | —     | 0.66  |
| Blansko .....                       | Berzelius ....          | 26.91 | 23.22 | 43.12 | 1.59 | 0.09  | 0.56  |
| Ohaba .....                         | Bukeisen ....           | 26.12 | 21.52 | 47.82 | 2.75 | —     | 9.18  |
| Pillistfer .....                    | Grewingk and<br>Schmidt | 28.02 | 22.09 | 42.99 | 2.99 | —     | 0.01  |
| Dundrum .....                       | Haughton ....           | 27.55 | 20.45 | 44.74 | 1.58 | —     | 0.44  |
| Hessle (large stone)                | Lindström ....          | 26.26 | 21.28 | 43.57 | 3.29 | 0.03  | 0.50  |
| " (small stone)                     | Nordenskiöld..          | 26.43 | 23.07 | 41.37 | 3.30 | trace | trace |
| Orvinio (chondritic<br>ground-mass) | L. Sipőcz ....          | 26.09 | 21.28 | 43.29 | 3.16 | —     | —     |
| Ditto (black ground-<br>mass)       | L. Sipőcz ....          | 26.65 | 20.18 | 42.55 | 4.71 | —     | —     |
| Stålldalen (grey<br>ground-mass)    | Lindström ....          | 25.66 | 21.41 | 44.83 | 2.73 | 0.26  | 0.20  |

| Locality.                           | Analyst.                | Ca.   | Al.  | Na.  | K.    | Cr.  | Sn.  |
|-------------------------------------|-------------------------|-------|------|------|-------|------|------|
| Erleben .....                       | Stromeyer ....          | 2.13  | 1.31 | 0.85 | —     | 0.26 | —    |
| Lixna .....                         | A. Kuhlberg ..          | trace | 2.12 | 0.83 | trace | 0.50 | —    |
| Blansko .....                       | Berzelius ....          | 1.02  | 1.85 | 0.85 | 0.25  | 0.42 | 0.12 |
| Ohaba .....                         | Bukeisen ....           | —     | 0.23 | 1.12 | —     | 0.26 | —    |
| Pillistfer .....                    | Grewingk and<br>Schmidt | 0.53  | 2.07 | 0.39 | 0.81  | 0.53 | 0.14 |
| Dundrum .....                       | Haughton ....           | 2.09  | 0.70 | 0.72 | 0.66  | 1.07 | —    |
| Hessle (large stone)                | Lindström ....          | 1.97  | 1.94 | 1.05 | —     | 0.08 | 0.03 |
| " (small stone)                     | Nordenskiöld..          | 2.28  | 1.27 | 1.78 | —     | 0.49 | 0.01 |
| Orvinio (chondritic<br>ground-mass) | L. Sipőcz ....          | 2.46  | 1.75 | 1.59 | 0.38  | —    | —    |
| Ditto (black ground-<br>mass)       | L. Sipőcz ....          | 2.56  | 1.91 | 1.10 | 0.34  | —    | —    |
| Stålldalen (grey<br>ground-mass)    | Lindström ....          | 1.77  | 1.74 | 0.71 | 0.18  | 0.42 | —    |

From the above table, it appears that a remarkable resemblance exists in the chemical composition of the meteorites, consequently it is highly probable that they had a common origin, having been originally either completely metallic or completely oxidised, their present composition being due to subsequent oxidation or reduction. Nordenskiöld is of opinion that other similar groups of meteorites may be arranged.

C. A. B.

## Organic Chemistry.

**Aluminium Iodine Reaction.** By J. H. GLADSTONE and A. TRIBE (*Chem. News*, 42, 2—3).—Water, alcohol, and ether, although not acted on by either aluminium or iodine, are readily attacked when these bodies act conjointly on them. Water at first forms a definite hydrate with aluminium iodide, but in presence of excess of the metal it is decomposed, hydrogen being evolved and aluminium hydrate formed.

Alcohol is similarly decomposed by aluminium and its iodide, with formation of aluminium ethylate and aluminium iodoethylate, hydrogen being evolved at the same time. Ether is attacked only by a mixture of iodine and aluminium, ethyl iodide and aluminium iodoethylate being formed. Similar reactions take place with amyl ether and ethyl and amyl acetates. Zinc and iron cannot be substituted for aluminium, but the chloride or bromide may be used instead of the iodide.

To decompose the alcohol, a small quantity of iodine (which is capable of decomposing a large quantity of the alcohol) is dissolved in it, the required excess of aluminium added, and the mixture is heated. Hydrogen is then evolved, and the reaction continues until all the aluminium is dissolved. By this means the ethylate, normal propylate, isobutylate, amylate, benzylate, phenylate, cresylate, and thymolate of aluminium have been obtained. Of these the first four may be distilled in a vacuum, but the other undergoes decomposition when distilled.

Methyl alcohol is not decomposed by a mixture of aluminium and its iodide, but in presence of free iodine, hydrogen is slowly evolved. An aluminium-platinum couple may be substituted for the metal.

Pseudopropyl alcohol is attacked under any circumstances.

Cetyl alcohol is slowly decomposed below 200°, above which temperature a secondary reaction sets in, cetyl iodide and aluminium hydrate being formed.

Allyl alcohol is at first decomposed in a similar manner to the alcohols of the series  $C_nH_{2n+1}.OH$ , but afterwards a portion of the hydrogen set free acts on the excess of alcohol, forming propylene and water.

Ethylene alcohol is only very slightly acted on by the reagent.

Propenyl alcohol is decomposed above 140°, with the formation of allyl iodide, aluminium hydrate, and free iodine; but when excess of



aluminium is present, no iodine is set free. No hydrogen is liberated. Hydrogen is not liberated from aldehyde.

It is seen, therefore, that aluminium is substituted for the basic hydrogen of water in monohydric alcohols, pseudopropyl alcohol being excepted; whilst in the di- and tri-hydric alcohols, aluminium is not substituted for the hydrogen, as is also the case with aldehyde. In the case of the ethers and of glycerol, the iodides of the positive radicals are formed.

The aluminium alcohols are solids, melting to clear liquids and remaining fluid at temperatures far below their melting points; those of the fatty series are capable of distillation. They are more or less soluble in alcohol, ether, and benzene, and are decomposed by water into the alcohol and aluminium hydrate. Their specific gravities at 4° are: ethylate, 1.147; propylate, 1.026; butylate, 0.988; amylate, 0.980; phenylate, 1.25; cresylate, 1.166; and thymolate, 1.04.

They are decomposed by heat, being resolved into the alcohol, and its olefine and alumina, and at the same time into alumina and the ether. Aluminium ethylate is decomposed mainly according to the first reaction:  $(C_2H_5O)_3Al_2 = Al_2O_3 + 3C_2H_4 + 3C_2H_5O$ , where as the phenylate yields chiefly the ether  $(C_6H_5O)_3Al_2 = Al_2O_3 + 3(C_6H_5)_2O$ : other reactions take place, yielding new compounds not yet investigated. The thymolate is decomposed into alumina, propylene, and bodies of the cresyl group, one of which is obtained in pearly plates by sublimation or crystallisation from alcohol; it appears to be an ether having the formula  $C_{14}H_{18}O$ , but is under investigation.

The reaction which takes place in the above decomposition is probably as follows: first, the aluminium iodide decomposes the alcohol with liberation of hydriodic acid, which is decomposed by the metallic aluminium present with evolution of hydrogen, and the iodide formed acts on a further quantity of alcohol, setting free more hydriodic acid, and so the reaction continues until all the metallic aluminium is dissolved, according to the equations—

- (1)  $6(C_nH_{2n-7}OH) + Al_2I_6 = Al_2(C_nH_{2n-7}O)_6 + 6HI$ ; and
- (2)  $6HI + Al_2 = Al_2I_6 + 3H_2$ .

L. T. O'S.

**Action of Bromine on Dichlorhydrin and Propylphycite.** By A. CLAUS and R. LINDHORST (*Ber.*, 13, 1209—1212).—When dichlorhydrin is heated with bromine (3 mols.) and water in sealed tubes at 110—120° until the colour of the bromine disappears, dibromodichloracetone is formed in the following way:  $C_3H_5Cl_2O + 3Br_2 = C_3H_5Br_2Cl_2O + 4HBr$ .

Dibromodichloracetone forms a hydrate with water, which on cooling may be obtained in well-formed crystals; these lose their water when kept over sulphuric acid. The anhydrous substance crystallises in bundles of leaflets, which may be melted by the warmth of the hand. It may be distilled in a vacuum without decomposition.

If, after the formation of the above compound, the heating is continued, then *tribromomonochloracetone*,  $C_3H_5Br_3ClO$ , is obtained in the form of prismatic needles; these after being separated mechanically from the dibromodichloracetone and recrystallised, melt at about 50°.

By continued heating, it was formerly supposed (Lindhorst, *Dissert.*, Freiburg, 1877) that a tetrabromacetone was formed; further investigation has, however, shown that it is a condensation product.

Dibromodichloracetone is easily decomposed by baryta-water in the cold, giving a yellow precipitate, which by the action of hydrochloric acid, gives formic and glycollic acids, the products of decomposition of the acid existing in the yellow precipitate as a barium salt. This decomposition shows the constitution of dibromochloracetone to be  $\text{CH}_2\text{Cl.CO.CBr}_2\text{Cl}$ .

The authors conclude that when bromine acts on dichlorhydrin, acetone is first formed, and that the hypothetical bromodichlorhydrin, from which propylphycite is obtained, does not exist. P. P. B.

**Fermentation of Glucose.** By L. BOUTROUX (*Compt. rend.*, 91, 236—238).—In a previous paper (this Journal, 36, 566) the author states that by sowing the ferment *Mycoderma aceti* in a solution of glucose, lactic acid is produced; on further examination of the acid, however, he finds that in all its reactions it corresponds to the gluconic acid of Hlasiwetz and Habermann (*Annalen*, 155, 123); its formula is identical,  $\text{C}_6\text{H}_{12}\text{O}_7$ , but its calcium salt contains 1 instead of 2 mols.  $\text{H}_2\text{O}$ .

This reaction is not fermentation properly so called, but merely oxidation, since every molecule of glucose absorbs 1 atom of oxygen.

L. T. O'S.

**Fermentation of Glucose.** By MAUMENÉ (*Compt. rend.*, 91, 331).—The author states that in his *Traité théorique et pratique de la fabrication du sucre*, he shows that the gluconic acid of Boutroux (previous Abstract) is produced by the oxidation of glucose by copper acetate, mercuric oxide, &c. From his experiments, he finds that the acid contains a molecule of oxygen more than Boutroux gives in his formula. He has not published his results.

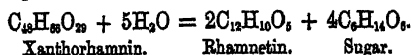
L. T. O'S.

**Chemistry of Sugar** (*Dingl. polyt. J.*, 237, 146—153).—Horsin-Déon examined palm-sugar from Calcutta with the following results:—

|                                      |       |
|--------------------------------------|-------|
| Cane-sugar.....                      | 87.97 |
| Reducing sugar.....                  | 1.71  |
| Gum .....                            | 4.88  |
| Water and volatile constituent ..... | 1.88  |
| Ash.....                             | 0.50  |
| Mannite, and loss .....              | 3.06  |

The sugar was fermenting.

Liebermann and Hörman have examined the glucoside from Persian berries, and represent its decomposition thus:—



Xanthorhamnin. Rhamnetin. Sugar.

They succeeded in obtaining beautiful crystals of the sugar, which analysis showed to be identical with isodulcite. Its rotatory power is given by—

$$[\alpha]_D = + 8.07^\circ.$$

Hönig and Rosenfeld have obtained a compound of grape-sugar and sodium,  $C_6H_{11}NaO_6$ , by decomposing an alcoholic sugar solution with alcoholic sodium.

E. Demole has effected a partial synthesis of milk-sugar. Milk-sugar was decomposed into galactose and lactoglucose by means of dilute acid, and the mixture was treated at the boiling point with acetic anhydride. The resulting ether was saponified with baryta; the product after repeated crystallisation from alcohol agreed with milk-sugar in all its properties. An analogous experiment with cane-sugar did not succeed.

V. Lippmann has investigated the inversion of cane-sugar by means of carbonic anhydride, and has found that with dry gas and sugar no inversion takes place. A sugar solution of  $+100^\circ$  saturated with carbonic anhydride showed after 150 days a rotation of  $-44.2^\circ$ ; the inversion was thus complete. The inverting power of carbonic anhydride is considerably increased by strong pressure. A solution of  $100^\circ$  saturated with the gas under pressure and heated, is completely inverted in 20 to 30 minutes.

By the action of zinc chloride on fused sugar, the author obtained a liquid which by fractional distillation yielded aldehyde, acetone, metacetone, formic acid, acetic acid, furfural, and apparently mesetyl oxide. Besides these, carbonic anhydride, carbonic oxide, hydrocarbon, ethylene and propylene were observed. In the neck of the retort small, pure white, hard crystals were found, which had a melting point of  $150^\circ$ , and which by analysis agreed with hexmethylbenzene,  $C_6(CH_3)_6$ .

Durin has found that in a solution of cane-sugar containing invert sugar, no inversion of the cane-sugar takes place at a temperature of  $70^\circ$  to  $75^\circ$ , when the alkalinity is maintained about that of  $.001$  of  $CaO$ . When heated to from  $75^\circ$  to  $114^\circ$ , the solution becomes faintly acid, and the inversion begins and goes on until completed. If the solution is maintained alkaline, no inversion takes place. The presence of invert sugar is not necessary, the inversion taking place without it on formation of the acid.

Wachtel finds that the arabic acid of the beet is not separated by lime and filtration, but forms an arabate which must be found in the molasses.

F. Weyer has found tricarballylic acid in the residue of Robert's apparatus, and has obtained it pure by Lippmann's process. The same author has obtained vanillin from many raw sugars by agitating an acid solution of the sugar with ether.

Lippmann finds the composition of tribasic calcium saccharate to be—



J. T.

**Decomposition-products of Sugar.** By E. REICHARDT and others (*Bied. Centr.*, 1880, 559).—By the action of bromine on cane-sugar, one-third is converted into gluconic acid, one-third into glucose, and the remainder into gum. By allowing a thin stream of melted sugar to fall on heated chloride of zinc, Lippmann observed that a very violent reaction set in, aldehyde, acetic acid, furfural and other

products being formed, together with hexmethylbenzene, a body having a melting point of  $150^{\circ}$ , and boiling point of  $258-260^{\circ}$ .

J. K. C.

**Saculmic Acid** (*Gazzetta*, 10, 240—245), and **Saculmin** (*ibid.*, 355—361). By F. SESTINI—This acid is obtained by treating crude saculmin (this vol., p. 538) with a cold dilute solution of potash or soda, filtering and precipitating; the precipitate is washed and dried over sulphuric acid. It then forms lustrous black fragments, sparingly soluble in water, easily in dilute alcohol, but almost insoluble in absolute alcohol. It may be purified by fractionally precipitating its alcoholic solution with ether. Its solutions are precipitated by baryta, by hydrochloric acid, or by sodium chloride. When heated to  $100^{\circ}$ , it is altered, and is no longer completely soluble in dilute alcohol or in potash solution. The results of the analyses correspond with the formula  $C_{11}H_{10}O_4$ , so that its formation may be represented by  $C_{12}H_{24}O_{12} = C_{11}H_{10}O_4 + H.COOH + 6H_2O$ . The silver compound obtained on adding silver nitrate to an alcoholic solution of saculmic acid exactly neutralised with potash, had the formula  $C_{11}H_9AgO_4$ . *Barium saculmate*,  $C_{22}H_{18}BaO_8 + H_2O$ , was thrown down as a brown precipitate on adding baryta-water to a solution of saculmic acid.

*Saculmin*.—The residue left after the crude saculmin had been treated with cold potash solution, as above mentioned, is partly soluble in hot 5 per cent. potash solution; this portion the author calls *saculmous acid*, and the insoluble residue *saculmin*. Analysis shows that saculmous acid contains more carbon and less hydrogen than saculmic acid. Saculmin after treatment with dilute hydrochloric acid has the composition  $C_{11}H_{10}O_4$ , and may be regarded as an anhydride derived from 4 mols. saculmic acid,  $C_{11}H_{10}O_4$ , by elimination of 1 mol.  $H_2O$ . It has a strong affinity for bases, taking up potash and baryta from their solutions; these combinations are not decomposed even by prolonged washing with distilled water.

C. E. G.

**Action of Glycerol on Starch.** By K. ZULKOWSKI (*Ber.*, 13, 1395—1398).—Since glycerol at  $190^{\circ}$  is capable of dissolving 6 per cent. of powdered starch and converting it into the soluble modification, soluble starch may be easily prepared by heating potato starch with glycerol at  $180-190^{\circ}$  for half an hour (if rice or wheat starch is used, the conversion takes place much more slowly). The solution is allowed to cool down to  $120^{\circ}$ , when it is poured into three times its volume of strong alcohol.

The precipitated starch is washed with alcohol first by decantation and then on a cotton filter with the aid of a filter-pump until it is free from glycerol. It may be further purified by solution in warm water, and reprecipitation by alcohol.

This soluble starch appears to be identical with Maschke's preparation (*Gmelin Kraut*, 4, 540), since its solution is powerfully dextrogyrate, and the substance loses its solubility when dried.

The concentrated aqueous solution slowly deposits insoluble starch.

Dilute solutions are precipitated by lime and baryta-water, and are coloured blue by iodine.

W. C. W.

**Nature of the Sugar in the Liver.** By J. SEEGEN and F. KRATZSCHMER (*Pflüger's Archiv.*, 22, 206—214).—The object of this paper is to combat the assertion of Musculus and Mering (*Zeitsch. f. Physiol. Chem.*, 2) that maltose is found in the liver. A preliminary experiment is described, in which the extract obtained, when examined by fermentation, reduction, and the polariscope, gave evidence only of the presence of grape-sugar.

The method of extracting the sugar by fractional precipitation as used by Musculus and Mering is described at length, and the results of experiments by this method are given; no evidence of any other sugar than grape-sugar could be obtained. Then follow the details of experiments with cold liver extract. The first series yielded the same result as before. A second and third series gave such a high specific rotation that the presence of maltose was suspected. The authors, however, give a different explanation of this high specific rotation. The figures were obtained from the liquids which had been fermented, and the results of experiments are given which show that dextrin in the presence of grape-sugar and yeast readily ferments, and that a body is formed having a very high specific rotation, which reduces copper solutions energetically. A large number of experiments were also made by dialysis. The dialysate was examined by fermentation, reduction of copper solution, and the polariscope, and again after treatment with hydrochloric acid: all the results tend to show that grape-sugar alone was present, and to this view the authors therefore adhere.

W. N.

**Maltodextrin.** By A. HERZFELD (*Bied. Centr.*, 1880, 347—350).—Experiments on the saccharification of starch by means of diastase having raised some doubts respecting the formulæ of the products formed, the author instituted those mentioned in the present article in order to obtain further information on the subject. The results of his labours show that saccharification of starch by diastase always produces dextrin through the series of amylo-, erythro-, and achroodextrin; at the same time a part of the achroodextrin is transformed into maltodextrin and maltose. This transformation takes place within certain limits. The absence of a sufficient quantity of sugar arrests the process, which is however resumed when the fermentation is allowed to proceed in the produced sugar. The temperature must be under 65°; if higher, and up to 80°, the diastase operates only as far as the erythro- and malto-dextrin stage, it being uncertain if achroodextrin and maltose will be produced. These conclusions coincide with those of Payen, by whom, however, maltodextrin was only considered a transition product.

The view of Musculus, that the starch molecule splits up into sugar on the one side and dextrin on the other, finds further refutation in these experiments, for, as shown by Bondonneau, both maltose and maltodextrin are produced by the action of diastase on dextrin quite free from starch. The theory must therefore be set aside until some satisfactory evidence is brought in its favour.

J. F.

**Preparation of Lauric, Myristic, Palmitic, and Stearic Aldehydes.** By F. KRAFFT (*Ber.*, 13, 1413—1418).—*Lauric aldehyde*,

$C_{12}H_{24}O$ , is prepared by subjecting to dry distillation under a pressure of 15–25 mm. a mixture of calcium or barium formate (3 parts) and laurate (2 parts), to which a small quantity of calcium carbonate has been added to diminish the fusibility. If the distillation is not carried on too far, the distillate can be easily purified by rectification under diminished pressure, after it has been freed from oily impurities by lying on porous plates. After recrystallisation from ether it forms glistening plates, which melt at  $44.5^{\circ}$  and boil at  $143^{\circ}$  under 22 mm. pressure.

*Myristic aldehyde*,  $C_{14}H_{28}O$ , obtained by a similar process, melts at  $52.5^{\circ}$ , and boils at  $169^{\circ}$  under 22 mm. pressure.

*Palmitic aldehyde*,  $C_{16}H_{32}O$ , crystallises in pearly plates, which melt at  $58.5^{\circ}$  and boil at  $193^{\circ}$  under 22 mm. pressure. The body previously known as cetyl aldehyde appears to be merely impure cetyl alcohol.

*Stearic aldehyde*,  $C_{18}H_{36}O$ , melts at  $63.5^{\circ}$  and boils at  $213^{\circ}$  under 22 mm. pressure, and at  $261^{\circ}$  under 100 mm. pressure. It crystallises in plates, which exhibit a bluish lustre.

W. C. W.

**Monobromacetone and the Alcohol of Acetone.** By A. EMERLING and R. WAGNER (*Annalen*, 204, 27–49).—The main object of the authors was to obtain from acetone a body which they name *acetol*,  $CH_3CO.CH_2OH$ , by the action of silver oxide or an alkaline carbonate on monobromacetone. The monobromacetone was prepared by acting on 100 grams of acetone with 138 grams of bromine. At first one drop of bromine was added to start the reaction, and then the rest was drawn through in the form of vapour mixed with air by means of an aspirator. The next step was to replace the bromine by the OH group, by acting on the monobromacetone with silver oxide and water. A volatile oil was thus obtained, which has a strong reducing action on Fehling's solution, and which the authors believe to be acetol; but they failed to separate it from the water with which it was combined. In the attempts to effect the dehydration of acetol, small quantities of an oily liquid with high boiling point, of the formula  $C_3H_6O_2 + xH_2O$ , were obtained, and also a second one having the composition  $C_3H_6O$ , but which is not identical with acetone or other known compounds. The first of these is probably propylene glycol, which on further dehydration is converted into  $C_3H_4O$ . In the preparation of acetol an acid was also obtained, which has a composition answering to the formula  $C_{12}H_{18}O_7$ .

*Action of Potassium Carbonate on an Aqueous Solution of Monobromacetone.*—100 grams of monobromacetone were heated at  $65^{\circ}$  for a day and a half with 70 grams of potassium carbonate dissolved in 100 grams of water. On filtering and distilling, a liquid of strongly reducing power was obtained. A part of this was submitted in sealed tubes to the action of freezing mixtures, and this yielded a stronger solution of acetol, which again became more concentrated when distilled at  $50^{\circ}$  to  $60^{\circ}$  in a vacuum. The strongest solution of acetol which the authors succeeded in obtaining was estimated to contain not more than 11 per cent.

The experiments have shown that acetol is very soluble in water,

to which it imparts a pleasant odour and a nut-like taste. It boils at above  $100^{\circ}$ , and is volatile in steam. Its specific gravity is greater than that of water. When distilled, it yields a liquid containing more water and a residue richer in acetol. When a frozen solution thaws, the portion which first liquefies contains more acetol than the rest. Evaporated over sulphuric acid it leaves no residue. Solutions of acetol reduce alkaline solutions of copper oxide with separation of the red suboxide: they also reduce ammoniacal solutions of silver and bismuth oxides on boiling. The solution of pure acetol has a neutral reaction, but on boiling with water an acid body is formed. Strong dehydrating agents, such as copper sulphate and calcium chloride, destroy acetol. Bases such as lime and baryta, and also potassium carbonate, decompose it with formation of an acid, especially on warming. On oxidation with potassium dichromate and dilute sulphuric acid, it yields acetic and carbonic acids. G. T. A.

**Action of Ethylamine and Diethylamine on Acetone.** By O. EPPINGER (*Annalen*, 204, 50—67).—By the action of ammonia on acetone, Heintz obtained a number of compounds, the most important of which were diacetoneamine, triacetoneamine, and dehydrotriacetoneamine (this *Journal*, 1874, 1081; and 1875, 351). It seemed probable, therefore, that similar reactions would take place between amines and acetone.

Ethylamine and diethylamine were not found to behave towards acetone in a manner analogous to ammonia, for ethylamine alone forms a base, and one only, ethyldiacetoneamine, corresponding with diacetoneamine, whilst ethyltriacetoneamine and its dehydro-compound either do not exist at all, or could not be obtained by the author's methods.

Diethylamine acts towards acetone in a manner analogous neither to ammonia nor to dimethylamine. In fact it seems that the capacity of acting with the amines on acetone decreases as their number of carbon atoms increases. Phenylamine, for instance, was found by Pauly (*Annalen*, 187, 198) to have no action on acetone. G. T. A.

**Vapour-densities of Anhydrous and Hydrated Formic and Acetic Acids.** By O. PETERSON and G. EKSTRAND (*Ber.*, 13, 1191—1195).—In this investigation the authors have used a method similar in principle to that of Dumas, but combining the accuracy of Bunsen's thermostatic method.

A vessel, A, made from thin glass tubing, closed at one end, and having a thin glass tube sealed to the other, is weighed filled with air, and then with the vapour of the body experimented on. Its capacity is ascertained by weighing it, filled up to a mark on the narrow tube, with water free from air. It is then filled with dry air and weighed, and thus the weight of water and its volume found. The narrow tube is drawn out into a capillary above the mark. A similar apparatus, A<sub>1</sub>, is made, and used as a tare for A. Both are filled with dry air, brought on to the pans of a balance, and equilibrium carefully established. A is then suspended in a tube containing the liquid, at the temperature of the vapour of which the determination is

*Formic Acid.*

| In vapour of    | T°.                         | Pure acid.<br>B. p. 100.5°.  | T°.                      | Acid + 1.262 p. c.<br>H <sub>2</sub> O. B. p. 101—<br>101.5°. | T°.                      | Acid + 2.02 p. c.<br>H <sub>2</sub> O. B. p. 101.2<br>—101.5°. | T°.                | Acid + 10.58 p. c.<br>H <sub>2</sub> O. B. p. 105.3<br>—105.4°. |
|-----------------|-----------------------------|------------------------------|--------------------------|---|--------------------------|--|--------------------|---|
| Toluene ..      | {<br>111.5<br>111.78<br>160 | {<br>2.987<br>2.979<br>1.824 | {<br>111.1<br>—<br>161.0 | {<br>2.215<br>—<br>1.705                                      | {<br>111.1<br>111.0<br>— | {<br>2.193<br>2.189<br>—                                       | {<br>—<br>161<br>— | {<br>—<br>1.430<br>—  |
| Turpentine ..   | {<br>160<br>214             | {<br>1.809<br>1.625          | {<br>—<br>214.0          | {<br>—<br>1.584   | {<br>—<br>—<br>—         | {<br>—<br>—<br>—   | {<br>—<br>214<br>— | {<br>—<br>1.428<br>—  |
| Nitrobenzene .. | {<br>214<br>214             | {<br>1.63<br>1.622           | {<br>—<br>—              | {<br>—<br>—   | {<br>—<br>—              | {<br>—<br>—  | {<br>—<br>—        | {<br>—<br>—   |

*Acetic Acid.*

| In vapour of    | T°.                          | Pure acid.<br>B. p. 117.1°. | T°.                    | Acid + 1.13 p. c.<br>H <sub>2</sub> O. B. p. 114.9<br>—115.1°. | T°.                  | Acid + 1.945 p. c.<br>H <sub>2</sub> O. B. p. 115.1°. | T°.                  | Acid + 8.414 p. c.<br>H <sub>2</sub> O. B. p. 108.5<br>—109.0°. |
|-----------------|------------------------------|-----------------------------|------------------------|--|----------------------|---|----------------------|---|
| Turpentine ..   | {<br>157.5<br>160.9<br>161.1 | {<br>2.747<br>2.64<br>2.62  | {<br>161<br>160.1<br>— | {<br>2.527<br>2.570<br>—                                       | {<br>160.8<br>—<br>— | {<br>2.501<br>—<br>—                                  | {<br>160.5<br>—<br>— | {<br>2.298<br>—<br>—  |
| Nitrobenzene .. | {<br>214<br>214              | {<br>2.220<br>2.217         | {<br>214<br>214        | {<br>2.14<br>2.157   | {<br>—<br>—          | {<br>—<br>—   | {<br>214<br>—        | {<br>2.122<br>—   |



to be made. In this it is heated for some minutes, and then sealed. It is finally weighed, after washing with alcohol, drying, and cooling, using A as tare. The end of the capillary of A is then cut off, and the liquid introduced into it. It is then heated as above, and soon becomes filled with the vapour of the liquid, some of which condenses in the capillary; to remove this a cylindrical piece of platinum foil attached to a copper wire, is heated and passed over the capillary. When all is vaporised the capillary is sealed, and the tube, when cold, is washed with alcohol, dried, and weighed. In this manner, the weights of the volumes of air and vapour filling A at a certain temperature are obtained, from which the vapour-density may be calculated. Further, the temperature of observation may be calculated from the weight of air in A at that temperature.

The tables (p. 869) contain the results of observations made with acetic and formic acids, containing varying amounts of water. These show that in case of formic acid addition of water increases the boiling point, whilst with acetic acid the opposite takes place; also that water decreases the vapour-density of these acids. P. P. B.

**Butyl and Isobutyl Hippurates.** By G. CAMPANI and D. BIZZARRI (*Gazzetta*, 10, 257—260).

*Isobutyl hippurate*,  $\text{COPh.NH.CH}_2\text{COO(CH}_2\text{.CHMe}_2\text{)}$ , prepared by the action of isobutyl iodide on silver hippurate, crystallises in minute transparent, rhombic prisms (m. p.  $45-46^\circ$ ), having an odour of aniseed, and a persistent bitter taste. It is insoluble in water, but soluble in alcohol, ether, benzene, and chloroform.

*Normal butyl hippurate*,  $\text{COPh.NH.CH}_2\text{COO(CH}_2\text{)}_3\text{CH}_3$ , prepared in the same way, crystallises with greater difficulty than its isomeride. It forms quadratic prisms (m. p.  $40-41^\circ$ ), resembling the isobutyl compound in odour and taste, and also in its solubility. It is saponified by the action of potash.

The author draws attention to the fact that, like many other ethereal salts of carboxylic acids, the melting point becomes lower as the alcoholic radicle becomes more complex.

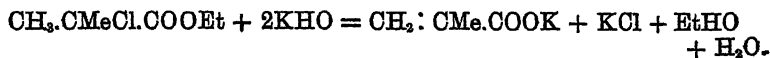
|                         | Melting point. |
|-------------------------|----------------|
| Methyl hippurate .....  | $80.5^\circ$   |
| Ethyl           " ..... | 60.5           |
| Isobutyl       " .....  | 45.5           |
| Butyl           " ..... | 40.5           |
| Isoamyl       " .....   | 27.5           |

C. E. G.

**Action of Potash on Ethyl Isochlorobutyrate.** By A. TESTA (*Gazzetta*, 10, 377—383).—Balbiano (this Journal, 36, 615) found that when ethyl isochlorobutyrate was decomposed with baryta in dilute solutions, hydroxybutyric acid was formed as the principal product of the reaction, but at the same time a secondary reaction gave rise to dibutylactic acid, and a small quantity of another acid which combined readily with bromine, perhaps methacrylic acid. The author's experiments were made with the object of ascertaining the nature of the second acid.

Ethyl isochlorobutyrate (4 parts) is allowed to drop slowly into a

boiling solution of potash (6 parts), in water (1 part). The product is then diluted with water, and after being boiled to expel the alcohol produced by the saponification, is treated with dilute sulphuric acid in slight excess, and agitated with ether. A dense white gelatinous precipitate, consisting of dibutylsuccinic acid, and a polymeride of methacrylic acid, is thus produced (see next abstract). This precipitate is filtered off, and the ethereal solution distilled to dryness, when a dense oily liquid is obtained, holding a little dibutylsuccinic acid in suspension; this may be separated by diluting with ether and filtering. After removal of the ether, the acids are neutralised with zinc oxide, and the sparingly soluble zinc hydroxybutyrate separated by crystallisation. The more soluble zinc salt is decomposed by sulphuretted hydrogen, the liberated acids neutralised with silver oxide, and the silver salts separated by fractional crystallisation from their solutions in water and alcohol. In this way the silver salts of *ethoxyisobutyric acid*,  $\text{CMe}_2(\text{OEt})\text{COOH}$ , and *methacrylic acid*,  $\text{CH}_2:\text{CMeCOOH}$ , can be isolated. The formation of these two acids may be represented by the following equations:—



C. E. G.

**Dibutylsuccinic Acid and a Polymeride of Methacrylic Acid.** By L. BALBIANO and A. TESTA (*Gazzetta*, 10, 373—377).—When ethyl isochlorobutyrate is saponified by boiling with aqueous potash-solution, and the liquid is acidified with sulphuric acid, and agitated with ether, a gelatinous white precipitate is produced, which consists of dibutylsuccinic acid, and a polymeride of methacrylic acid. To separate these, the precipitate, after being well washed with ether, is treated with hot water; the polymeride of methacrylic acid dissolves readily, whilst the dibutylsuccinic acid remains behind; by reprecipitating the solution with ether and again dissolving in warm water, repeating the operation once or twice, the polymeride may be obtained in a comparatively pure state; the dibutylsuccinic acid, however, obstinately retains traces of the polymeride. Both these substances closely resemble one another in physical characters, being amorphous, and when dry transparent and gelatinous, like isinglass.

*Dibutylsuccinic acid*,  $\text{COOH.CMe}_2\text{O.CMe}_2\text{COOH}$ , is not sensibly attacked by hot nitric acid, but is readily decomposed when fused with potash; the reaction has not been examined by the author further than to note that much potassium carbonate is produced.

The polymeride of methacrylic acid differs from that described by Engelhorn and Fittig, particularly in its reaction when fused with potash. The modification described by the author is readily decomposed under these circumstances, whilst Engelhorn and Fittig's is attacked with difficulty.

C. E. G.

**Octylic Aceto-acetate and its Derivatives.** By M. GUTZMANN (*Annalen*, 204, 1—14).—*Ethyl octylacetoacetate*,  $\text{C}_{14}\text{H}_{28}\text{O}_4$  or  $\text{CH}_3\text{CO.CH}(\text{C}_8\text{H}_{17})\text{COOEt}$ , is prepared by acting on ethyl aceto-

3 p 2

sodacetate with octyl iodide. It is a colourless oil (b. p. 280—282°, uncorr.), which refracts light strongly, and has a sp. gr. of 0.9304 (at 18.5°, compared with water at 17.5°). On saponification it yields octylacetone (normal methyl nonylketone), and octylacetic acid (caproic acid).

*Ethyl diocetylacetoacetate*,  $C_{22}H_{42}O_3$ , obtained by acting on ethyl acetosodacetate with octyl iodide, is a light colourless oil (b. p. 340—342°, uncorr.).

On saponification, it yields dioctylacetone and dioctylacetic acid, which is isomeric with stearic acid. Dioctylic or isostearic acid,  $C_{18}H_{36}O_2$ , differs from stearic acid in its melting point, 38.5°; that of stearic acid, according to Heintz (*Annalen*, **84**, 299), being 69.1—69.2°. When slowly crystallised from alcohol, it consists of fine, colourless, transparent plates. The *sodium* salt can be obtained as a white powder, which, when moistened, swells up to a gelatinous mass, easily soluble in water. The *barium* salt,  $(C_{18}H_{36}O_2)_2Ba$ , crystallises from alcohol in snow-white, matted needles, which in presence of moisture form a viscous mass. The *silver* salt,  $C_{18}H_{36}O_2Ag$ , is insoluble in water, and becomes blackened on exposure to light. The *ethyl* salt,  $C_{17}H_{35}.COOEt$ , prepared by saturating an alcoholic solution of the acid with hydrochloric acid gas, and adding water, is a colourless oil, which could not be crystallised by cooling to 0°. G. T. A.

**Two New Syntheses of Methyl-ethyl-hydroxyacetic Acid.** By E. BÖCKING (*Annalen*, **204**, 14—26).—(1.) From methyl-ethylketone, by heating it with an aqueous solution of hydrocyanic acid and hydrochloric acid, and extracting with ether, or better, by adding a little more than the calculated quantity of potassium cyanide, then a molecule of fuming hydrochloric acid, drop by drop, and finally, after addition of the same quantity of hydrochloric acid, heating on the water-bath.

Another method is to heat the ketone for a day with anhydrous hydrocyanic acid in a closed tube, at 70—80°.

Methyl-ethyl-hydroxyacetic acid,  $C_5H_{10}O_3$ , or  $CEtMe(OH).COOH$ , is very soluble, has a sour taste and reaction, and sublimes at 90° in fine, colourless, stellate groups of needles, which, when thrown into water, rotate rapidly during solution. The acid agrees in the above properties with the ethomethoxalic acid of Frankland and Duppa (*Annalen*, **135**, 36), but differs in melting point—63°, instead of 66°. The *silver* salt,  $C_5H_9O_3Ag$ , agrees in properties with the corresponding compound of Frankland and Duppa. The *barium* salt,  $(C_5H_9O_3)_2Ba$ , consists of colourless, soluble, silky masses. The *zinc* salt forms a bulky, white, crystalline precipitate. Methyl-ethyl-hydroxyacetic acid, when heated with fuming hydriodic acid, is decomposed with difficulty, yielding methylethylacetic acid.

(2.) From methylethylacetic acid, by converting it into  $\alpha$ -bromo-methylethylacetic acid, and heating the ethyl salt of the latter with sodium carbonate. G. T. A.

**Suberic Acid produced by Oxidation.** By F. GANTTER and O. HALL (*Ber.*, **13**, 1165—1170).—This acid was prepared by oxidising

| Name.                | Formula.                                  | Form.                                    | Solubilities in 100 parts of water (anhydrous salt). | Remarks.  |
|----------------------|---|--|--|---|
| Potassium .....      | $K_2C_8H_{12}O_4$ .....                   | —  | 84·66 at 14° .....                                   | —   |
| Sodium .....         | $Na_2C_8H_{12}O_4 + \frac{1}{2}H_2O$ .... | Wart-like, efflorescent mass..           | 49·91 at 14° .....                                   | —   |
| Ammonium .....       | $(NH_4)_2C_8H_{12}O_4$ .....              | Leaflets, resembling the potassium salt. | 87·83 at 25° .....                                   | By evaporation of an ammoniacal solution, in an atmosphere of ammonia.        |
| Ammonium hydrogen    | —   | —  | —  | Is decomposed into free acid by standing, or when dry by heating at 105—110°. |
| Barium .....         | $BaC_8H_{12}O_4$ .....                    | Coarse crystalline powder ..             | 2·19 at 7 5° .....                                   | —   |
| Strontium .....      | $SrC_8H_{12}O_4$ .....                    | —  | 2·9 at 14° .....                                     | —   |
| Calcium .....        | $CaC_8H_{12}O_4 + H_2O$ .....             | Crystalline powder .....                 | 1·9 at 100° .....                                    | —   |
| Magnesium .....      | $MgC_8H_{12}O_4 + 8H_2O$ ....             | Ill-defined .....                        | 0·62 at 14° .....                                    | —   |
| Aluminium (basic) .. | $Al_2O(C_8H_{12}O_4)_2$ .....             | White voluminous precipitate.            | 0·423 at 100° .....                                  | —   |
| Ferric (basic) ..... | $Fe_2O(C_8H_{12}O_4)_2$ .....             | A light-red precipitate .....            | 13·64 at 20° .....                                   | —   |
| Manganese .....      | $Mn(C_8H_{12}O_4)_2 + 8H_2O$ ..           | Shining reddish leaflets ....            | 0·0094 at 6·5° .....                                 | —   |
|                      |   |  | Most insoluble of all substrates.                    | —   |
|                      |   |  | 1·081 at 18° .....                                   | —   |

| Name.          | Formula.  | Form.  | Solubilities in 100 parts of water (anhydrous salt). | Remarks.  |
|----------------|---|--|--|---|
| Nickel .....   | $\text{NiC}_8\text{H}_{13}\text{O}_4 + 4\text{H}_2\text{O}$ ..... | Apple-green, ill-defined crystalline crust, or crystalline meal. | 0.791 at 7.5° .....<br>1.26 at 18° .....             | Dried at 100°, is yellowish-green; takes up water from the air.   |
| Cobalt .....   | $\text{CoC}_8\text{H}_{12}\text{O}_4 + 4\text{H}_2\text{O}$ ..... | Pale red leaflets, vitreous lustre.                              | 1.16 at 14° .....<br>1.98 at 18° .....               | Dried at 100°, is deep blue.  |
| —              | $\text{CoC}_8\text{H}_{12}\text{O}_4 + 2\text{H}_2\text{O}$ ..... | Purple-red coloured salt .....                                   | 0.85 at 100° .....                                   | By exposure of dried salt to the air, or precipitating $\text{CoCl}_2$ with sodium suberate.                      |
| Zinc .....     | $\text{ZnC}_8\text{H}_{12}\text{O}_4$ .....                       | Crystalline precipitate .....                                    | 0.041 at 14° .....                                   | —   |
| Cadmium .....  | $\text{CdC}_8\text{H}_{12}\text{O} + \text{H}_2\text{O}$ .....    | Crystallines in leaflets .....                                   | 0.08 at 17° .....                                    | —   |
| Copper .....   | $\text{CuC}_8\text{H}_{12}\text{O} + \text{H}_2\text{O}$ .....    | A bluish-green powder. ....                                      | 0.024 at 16° .....                                   | Dried it becomes green. ....  |
|                | $\text{CuC}_8\text{H}_{12}\text{O} + 2\text{H}_2\text{O}$ .....   | Ultramarine blue crystalline grains.                             | —  | Formed by exposure of $\text{Cu}(\text{C}_8\text{H}_{12}\text{O}_4) + \text{H}_2\text{O}$ to the action of water. |
| Lead .....     | $\text{PbC}_8\text{H}_{12}\text{O}$ .....                         | White, pulverulent precipitate.                                  | 0.008 at 16° .....                                   | —   |
| Silver .....   | $\text{Ag}_2\text{C}_8\text{H}_{12}\text{O}$ .....                | White precipitate not decomposed by action of light.             | 0.0075 at 8° .....                                   | —   |
| Mercuric ..... | $\text{HgC}_8\text{H}_{12}\text{O}$ .....                         | White, coarsely crystalline precipitate                          | 0.012 at 7.5° .....                                  | —   |

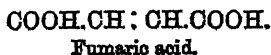
Mercurous salt, a white precipitate, appears to contain free acid.

palm oil with nitric acid; the product, after being repeatedly melted, was extracted with ether, as long as the portions sparingly soluble in ether, after crystallising from water, exhibited the melting point,  $135^{\circ}$ . This portion was then dissolved in ammonia, and fractionated by precipitating with calcium chloride. The second fraction yielded an acid (m. p.  $139^{\circ}$ ), which, after crystallisation from strong nitric acid, and then from water, exhibited the melting point,  $140^{\circ}$ , viz., that of pure suberic acid. From solutions containing sodium chloride, it crystallises in feathery crystals, resembling those of ammonium chloride. It distils about  $300^{\circ}$ , without decomposition, and is not volatilised by steam. 100 pts. of water dissolve 0.142 of the acid at  $15.5^{\circ}$ . The following salts have been prepared (see table, pp. 873 and 874).

Ethyl suberate is obtained by digesting 15 grams of suberic acid and 25 grams of alcohol, with 25 grams of concentrated sulphuric acid; it boils at  $280-282^{\circ}$ , is decomposed by boiling with soda, but only partially by aqueous ammonia. P. P. B.

**Trioxymaleic Acid.** By S. TANATAR (*Ber.*, 13, 1382—1388).—Trioxymaleic acid is prepared by oxidising a cold dilute solution of potassium maleate with a dilute solution of potassium permanganate. When the operation is finished, the manganese oxide is removed by filtration, and the filtrate is acidified with acetic acid and concentrated by evaporation. The solution is then boiled with calcium acetate and filtered. As the filtrate cools, rhombic prisms of calcium trioxymaleate are deposited, but several days are required for the complete separation of these crystals. A further yield of this salt may frequently be obtained by treating the residue, consisting chiefly of calcium oxalate, with boiling water. In order to prepare the free acid, calcium trioxymaleate is converted into the potassium salt by boiling with a solution of potash; and the lead salt obtained from the potassium salt by double decomposition is subjected to the action of sulphuretted hydrogen. *Trioxymaleic acid* is a thick colourless liquid which is converted at  $110^{\circ}$  into a brittle amorphous mass resembling glass in appearance. The dried acid dissolves freely in water and sparingly in alcohol. It melts at  $110^{\circ}$  and begins to decompose at  $180^{\circ}$ . This acid forms two uncrystallisable potassium salts, which are very soluble in water. Cadmium and barium trioxymaleates crystallise in rhombic prisms, freely soluble in hot water. The *zinc* salt,  $C_4H_2ZnO_7 + 2H_2O$ , forms transparent, lustrous, rhombic prisms, which are sparingly soluble. Silver trioxymaleate is amorphous. *Diethyl trioxymaleate*,  $C_4H_2Et_2O_7$ , is a colourless liquid of the consistency of honey. It is soluble in alcohol, ether, and water. The diacetic derivative of this ethereal salt,  $C_4Et_2Ac_2O_7$ , is a thick liquid which solidifies to a crystalline mass composed of silky needles (m. p.  $48^{\circ}$ ) when kept for several weeks.

The presence of two hydroxyl groups in this acid is evidence in favour of Fittig's views of the constitution of fumaric and maleic acids.



**Preparation of the Ethereal Salts of Tartaric and Racemic Acids.** By R. ANSCHÜTZ and A. PICTET (*Ber.*, 13, 1175—1178 and 1538). The chief difficulty in obtaining these ethers by the ordinary method is due to the fact that water decomposes them. The authors recommend treating the solution of the acid in alcohol with hydrochloric acid gas in the cold. The saturated solution is allowed to stand and then treated with a stream of dry air, and the alcohol and aqueous hydrochloric acid are removed by heating the solution under reduced pressure on the water-bath. The product so obtained is again treated in a manner similar to the free acid, and then after drying in the manner described is distilled under reduced pressure. By this method the following ethers have been prepared:—

*Dimethyl dextrotartrate*,  $C_2H_2(OH)_2(COOMe)_2$ , is a viscous, odourless, strongly-refractive liquid; has a sweet taste. After some time it suddenly assumes the solid state, forming a crystalline mass melting at  $48^\circ$ . The solid ether is easily soluble in alcohol, chloroform, and benzene, from which it may be obtained in well-formed crystals. Its sp. gr. at  $15^\circ$  is 1.3403, it boils at  $163^\circ$  under 23 mm. pressure, and at  $280^\circ$  under atmospheric pressure.

*Diethyl dextrotartrate*,  $C_2H_2(OH)_2(COOEt)_2$ , is a colourless, viscous liquid. Its sp. gr. is 1.2097 at  $14^\circ$ , it boils at  $162^\circ$  under 19 mm pressure, and at  $280^\circ$  under ordinary pressure.

*Dipropyl dextrotartrate*,  $C_2H_2(OH)_2(COOPr)_2$ , is a colourless liquid, more mobile than the ethyl salt. Its sp. gr. is 1.1392 at  $17^\circ$ , it boils at  $181^\circ$  under 23 mm. pressure, and at  $303^\circ$  under ordinary pressure.

A column 220 mm. long, with a Wild's polaristrobometer, gave the following results, the temperature being about  $18^\circ$ :—

|                      | Angle of rotation. | $[\alpha]_D$ . | M.      | Difference. |
|----------------------|--------------------|----------------|---------|-------------|
| Dimethyl ether ..... | + 5.40             | + 1.83         | + 3.26  | } 12.13     |
| Diethyl " .....      | + 19.88            | + 7.47         | + 15.39 |             |
| Dipropyl " .....     | + 30.80            | + 12.09        | + 28.20 |             |

The difference between the molecular rotatory power of the dimethyl and diethyl ethers is seen to be the same as that between the diethyl and dipropyl ethers.

*Dimethyl-racemate* forms a white crystalline mass, crystallising from alcohol in monoclinic crystals resembling augite; it melts at  $85^\circ$  and boils at  $282^\circ$  under ordinary pressure. Its alcoholic solution is optically inactive.

*Diacetyl-dextrotartaric anhydride*,  $C_2H_2(OAc)_2C_2O_3$ , melts at  $125$ — $129^\circ$  (Perkin,  $126^\circ$ ). Its benzene solution rotates strongly to the right. The aqueous or alcoholic solution of its syrupy acid hydrate is levogyrate, as are also the barium and sodium salts.

*Dibenzoyl-dextrotartaric anhydride*,  $C_2H_2(OBz)_2C_2O_3$ , forms small, white needles, easily soluble in alcohol, chloroform, and benzene. It melts at  $174^\circ$ . Alkalis and ammonia dissolve it, but it is insoluble in water.

*Diacetyl-racemic anhydride*,  $C_2H_3(OAc)_2C_2O_3$ , melts at 122—125°. It is optically inactive, as also is its aqueous solution. P. P. B.

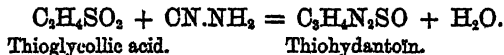
**Citric Acid.** By G. ANDREONI (*Ber.*, 13, 1394—1395).—By treating ethyl bromacetate with the product of the action of sodium on an ethereal solution of triethyl malate and distilling the mixture in a vacuum, a noncrystallisable syrupy liquid is obtained which the author believes to be ethylcitric acid. W. C. W.

**Propylneurine.** By H. G. MORLEY (*Compt. rend.*, 91, 333—334).—By heating propylene chlorhydrin with trimethylamine at 100° in sealed tubes propyleneneurine chloride,  $C_3H_5(HO).NMe_3Cl$ , is obtained. It forms colourless, transparent crystals, is very hygroscopic, and acquires a brown colour on exposure to light. Its platinumchloride crystallises in plates, insoluble in alcohol and ether, but soluble in water. By treating the chloride with moist silver oxide, a syrupy basic liquid is obtained, most probably the free base.

By heating propylene chlorhydrin with dimethylamine at 100° for some time a neutral liquid is obtained which yields a crystalline platinumchloride of the formula  $(C_3H_7OH.NMe)_2.2HCl.PtCl_4$ .

L. T. O'S.

**Synthesis of Thiohydantoin.** By R. ANDREASCH (*Ber.*, 13, 1421—1423).—Thiohydantoin thioglycollate is formed when an aqueous solution of cyanamide and thioglycolic acid is evaporated to dryness.



The residue is dissolved in water and the thiohydantoin precipitated by ammonia. W. C. W.

**Carbamideacetosulphonic Acid, a New Derivative of Thiohydantoin.** By R. ANDREASCH (*Ber.*, 13, 1423—1427).—*Potassium carbamideacetosulphonate*,  $NH_2.CO.NH.CO.CH_2.SO_3K$ , is formed by adding potassium chlorate in small quantities to 5 grams of thiohydantoin and 50 c.c. of hydrochloric acid (sp. gr. 1.08). The mixture is gently warmed to start the reaction, but if the evolution of chlorine takes place too rapidly, the temperature must be lowered; 4.2 grams of potassium chlorate are required for 5 grams of thiohydantoin. When the reaction is complete, the potassium salt slowly separates as a crystalline meal, which is freed as much as possible from the mother-liquor, washed with alcohol, and crystallised from warm water. It forms monoclinic plates, which require for solution 58.6 parts of water at 22° and 4.3 at 100°.

Potassium carbamideacetosulphonate is decomposed by nitrous acid with the formation of acid potassium acetosulphonate and carbonic anhydride,  $C_3H_5KN_2SO_3 + N_2O_3 = C_2H_5KSO_3 + CO_2 + 2N_2 + H_2O$ . W. C. W.

**Synthesis of Meta-isopropyltoluene.** By A. ZIEGLER and W. KELLER (*Ber.*, 13, 1399—1402).—The meta-isopropyltoluene, which is formed by treating a mixture of 500 grams of toluene and 100 grams



of isopropyl iodide with 40 grams of aluminium chloride, is identical with the cymene obtained from resin oil (*Ber.*, 13, 1157).

W. C. W.

**A New Cymene from Light Resin Oil.** By W. KELLE (*Ber.*, 13, 1157—1160).—Light resin oil when treated with soda is separated into two portions, one containing the salts of acids belong to the fatty series, and the other consisting of several hydrocarbons. On distillation, the latter gave a fraction boiling at 170—178°, and consisting of the new cymene. When it is heated with strong sulphuric acid, two sulphonic acids are produced, which may be separated by taking advantage of the difference in solubility of their barium salts in alcohol.

*Barium  $\alpha$ -cymene-sulphonate*,  $(C_{10}H_{14}SO_3)_2Ba + H_2O$ , crystallising in shining leaflets, is the less soluble salt; by treatment with phosphorus pentachloride and ammonia, it yields a sulphamide crystallising from water in leaflets (m. p. 73°).

*Barium  $\beta$ -cymene-sulphonate* is obtained from the filtrate from the above as an ill-defined crystalline mass. It separates as a crystalline powder from absolute alcohol in which it is easily soluble.  *$\beta$ -Cymene-sulphamide* crystallises from water in large, flexible, glistening leaflets, resembling naphthalene.

The cymene obtained from barium  $\alpha$ -cymene-sulphonate by heating it at 200° with hydrochloric acid, is a colourless, strongly refractive liquid, having an odour like cymene, and boiling at 173—175°. On oxidation it yields isophthalic acid, and since its  $\beta$ -sulphonic acid differs from that of metacymene, the author regards it as meta-isopropyltoluene.

P. P. B.

**Action of Bromine on Toluene and its Derivatives.** By C. L. JACKSON and A. W. FIELD (*Ber.*, 13, 1215—1216).—The authors have determined the amount of benzyl compounds formed by the action of bromine on toluene, parachlorotoluene, parabromo- and orthobromotoluene, at temperatures varying from 80° to a little above the boiling point of these compounds. These experiments show that at higher temperatures benzyl compounds are formed, and at lower substituted toluenes, as pointed out by Beilstein. The benzyl compounds form the chief product at temperatures near the boiling point of toluene; above this there is a slight increase for every increment of temperature, but the greatest increase takes place between 100° and 111°. Toluene takes up bromine more easily than its substituted derivatives; in the case of the monobromotoluenes the para-compound when treated with bromine forms benzyl derivatives more quickly than the meta, and this latter more quickly than the ortho. Finally, the authors find that the presence of iodine in toluene does not prevent the formation of benzyl bromide at high temperatures.

P. P. B.

**Parachlorobenzyl Compounds.** By C. L. JACKSON and J. WHITE (*Ber.*, 13, 1217—1218).—In a former communication one of the authors has shown the necessity of a revision of these compounds which have been studied by the following:—Böhler (*Annalen*, 154, 56), Vogt and Henninger (*ibid.*, 165, 372), Pauly (*ibid.*, 167, 187),

Beilstein (*ibid.*, 116, 336), Neuhoof (*ibid.*, 147, 339), and Naquet (*ibid.*, Suppl., 2, 249).

*Parachlorobenzyl bromide* (m. p.  $48.5^{\circ}$ ), treated with sodium sulphite, yields a sulphonic acid crystallising in quadrangular leaflets (m. p. about  $108^{\circ}$ ), which are very unstable, and its chloride melts at  $85.5^{\circ}$ . Sodium and potassium parachlorobenzylsulphonate crystallise without water, the barium salt with  $2H_2O$ , the calcium salt with 7 and  $2H_2O$ , the copper salt with  $2H_2O$ , the lead salt with 1 mol.  $H_2O$ , and the basic lead salt contains  $PbO_2.H_2.2H_2O$ .

*Parachlorobenzyl sulphide*,  $(C_6H_4Cl.CH_2)_2S$ , melts at  $42^{\circ}$ , the disulphide,  $(C_6H_4Cl.CH_2)_2S_2$ , at  $59^{\circ}$ : the mercaptan,  $C_6H_4Cl.CH_2.SH$ , at  $19^{\circ}(?)$ ; the sulphone,  $(C_6H_4Cl.CH_2)_2SO_2$ , at  $165^{\circ}$ ; and the disulphide dioxide,  $(C_6H_4Cl.CH_2)_2S_2O_2$ , at about  $120^{\circ}$ . The parachlorobenzyl ether,  $C_6H_4Cl.CH_2.OEt$ , is an oil.  
P. P. B.

**Orthobromobenzyl Compounds.** By C. L. JACKSON and J. F. WHITE (*Ber.*, 13, 1218—1219).—*Orthobromobenzyl bromide*,  $C_6H_4Br.CH_2Br$ , obtained by the action of bromine on boiling bromotolene, is purified by distilling in hydrobromic acid vapour; it crystallises in broad tablets (m. p.  $30^{\circ}$ ). From this the following derivatives have been obtained:—

*The alcohol*,  $C_6H_4Br.CH_2.OH$ , in white flat needles (m. p.  $80^{\circ}$ ).

*The cyanide*, a dark coloured oil, which yields, when saponified, *orthobromophenylacetic acid*,  $C_6H_4Br.CH_2.COOH$ . It crystallises in shining scales, or flat needles (m. p.  $102.5$ — $103^{\circ}$ )\*. Its calcium salt crystallises in radiating anhydrous needles; the barium salt is uncrystallisable.

*The thiocyanate*,  $C_6H_4Br.CH_2.SCN$ , is an oil.

*The primary amine*,  $C_6H_4Br.CH_2.NH_2$ , is an oil; its carbonate melts at  $95^{\circ}$ , and its chloride at  $208^{\circ}$ .

*The secondary amine*,  $(C_6H_4Br.CH_2)_2NH$ , melts at  $36^{\circ}$ , and its chloride at  $166^{\circ}$ .

*The tertiary base*,  $(C_6H_4Br.CH_2)_3N$ , melts at  $121.5^{\circ}$ , and its salts are ill defined.  
P. P. B.

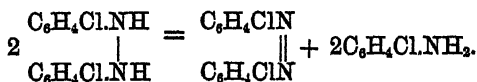
\* **Tetrabromodibenzylene-paradimethylphenylamine.** By G. MAZZARA (*Gazzetta*, 10, 370—372).—Dibenzylene-paradimethylphenylamine, prepared according to Schiff's method by the action of benzaldehyde on paratoluidine, is dissolved in carbon bisulphide, and a bisulphide solution of bromine is gradually added, taking care to keep the mixture cold. The canary-yellow precipitate which is produced is washed first with bisulphide and then with ether. The tetrabromo-derivative,  $(CHPh)_2(NC_6H_4Br_2Me)_2$ , thus obtained decomposes rapidly in contact with the air, and when heated it melts at  $160$ — $165^{\circ}$  with decomposition. It is very soluble in alcohol, and the solution when boiled undergoes decomposition. On cooling, long silky needles of a dibromotoluidine (m. p.  $73^{\circ}$ ) are deposited, whilst the solution contains benzaldehyde.  
C. E. G.

\* The Abstractor has shown that this acid is obtained by brominating phenylacetic acid, and found its melting point to be  $103$ — $104^{\circ}$  (this Journal, *Trans.*, 1880, 95).

**Action of Benzotrichloride on Primary Amines.** By J. H. STEBBINS (*Chem. News*, 24, 7).—By allowing benzotrichloride and paratoluidine to react on one another in equal molecular proportions, a violent action takes place, hydrochloric acid being evolved, and a white granular mass obtained soluble in alcohol, crystallising from the solution in needles (m. p. 115°) on slow cooling, and in rhombic prisms on rapid cooling. The crystals sublime at a temperature a little above their melting point; they are sparingly soluble in water and hydrochloric acid, but soluble in acetic acid. Sulphuric acid dissolves it with evolution of hydrochloric acid; by adding water to the solution, a precipitate is formed. By oxidation, a substance is obtained crystallising from alcohol in yellow needles. The author is continuing the research to ascertain the constitution of the body.

L. T. O'S.

**Substituted Azobenzenes.** By A. CALM and K. HEUMANN (*Ber.*, 13, 1180—1185).—*Paradichlorhydrazobenzene* (m. p. 122°), prepared by the action of zinc-dust and aqueous soda on parachloronitrobenzene, when heated with moderately concentrated hydrochloric acid, yields *paradichlorazobenzene*, m. p. 183° (*Ber.*, 8, 912), and *parachloraniline*, thus:—



*Paradibromohydrazobenzene* (m. p. 130°) is decomposed in a similar manner, forming *paradibromazobenzene* (m. p. 205°), and *parabromaniline* (m. p. 68°).

*Paradichlorazobenzene-monosulphonic acid*,  $\text{C}_{12}\text{H}_7\text{Cl}_2(\text{SO}_3\text{H})\text{N}_2$ , is obtained by heating *paradichlorazobenzene* with fuming sulphuric acid at 140—150°. It crystallises from hot water in fine reddish-yellow needles, which are soluble in cold water, but more easily in hot water and alcohol. Its sodium salt crystallises in shining golden leaflets. By reason of the insolubility of its salts, it decomposes chlorides and nitrates, but is precipitated from the solutions of its salts by hydrochloric and sulphuric acids.

*Mononitrodichlorazobenzene*,  $\text{C}_{12}\text{H}_7\text{Cl}_2(\text{NO}_2)\text{N}_2$ , is obtained by treating *nitroparachlorazoxybenzene*, m. p. 154° (*Ber.*, 5, 912), with alcoholic ammonium sulphide. It crystallises in pale yellow needles, is sparingly soluble in alcohol, and melts at 210°. The possibility of its being a hydrazo-derivative is excluded by its high melting point. Attempts to prepare it by nitrating *dichlorazobenzene* resulted in the formation of *mononitroparachlorazoxybenzene* (m. p. 133—134°).

P. P. B.

**Colouring Matters produced by the Action of Diazo-compounds on Phenols.** By J. H. STEBBINS (*Chem. News*, 42, 44).—*Azobenzene-trinitro-oxybenzene*, prepared by the action of diazobenzene nitrate on trinitrophenol, explodes violently on heating.

*Azobenzene-pyrogallol*, prepared by the action of azobenzene nitrate on pyrogallol, crystallises in red-brown needles, sparingly soluble in alcohol.

*Parazo-sulphoxyl-benzene-phloroglucinol* is obtained by acting on

diazosulphanilic acid with phloroglucinol. It forms a soda salt, readily soluble in water, and an acid barium salt which is sparingly soluble in water.

*Azobenzene-sulphocresol*, obtained by the action of cresolsulphonic acid on diazobenzene nitrate, crystallises in red-brown needles, soluble in alcohol, and sparingly soluble in hot water.

*Dinitro-oxy-azobenzene-orthoxysulphozybenzene*, obtained from diazo-dinitrophenol and phenol-ortho-sulphacid, crystallises in yellow-brown needles, having a metallic lustre, and sparingly soluble in hot and cold water.

*Azonaphthalene-sulphozyl-orthonitrozy-l-benzene* crystallises in red-brown microscopic needles, soluble in water; it is prepared by the action of diazonaphthionic acid on orthonitrophenol.

*Parazo-sulphozylbenzene-betaoxydisulphozyl-naphthalene*, obtained by treating diazosulphanilic acid with naphthalenedisulphonic acid, crystallises in orange-coloured leaflets, with a beetle-green lustre; it is soluble in water, and forms a lead salt, a yellow powder soluble in water.

*Azobenzene-disulphonaphthol* is prepared by treating the sodium salt of  $\beta$ -naphtholdisulphonic acid with diazobenzene nitrate; its soda salt is very soluble in water, and the barium salt only sparingly soluble.

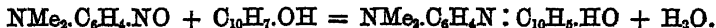
*Parazotoluene- $\beta$ -naphthol-disulphonic acid* is prepared by acting on diazotoluene nitrate with  $\beta$ -naphtholdisulphonic acid; it crystallises in red laminae, soluble in water, and dyes a scarlet colour. Its soda salt is very soluble in water; and its barium salt sparingly soluble. The ortho- and meta-compounds have been prepared; the former gives a more yellow, and the latter a redder shade than the para-compound.

*Parazosulphozyl-naphthalene-resorcinol*, obtained by the action of diazonaphthionic acid on resorcinol, forms dark-brown needles, very soluble in water.

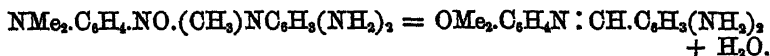
*Parazodibromo-sulphozylbenzene- $\beta$ -naphthalein*, obtained by treating paradiazodibromo-benzene-sulphonic acid with  $\beta$ -naphthol, is soluble in water.

L. T. O'S.

**Colouring Matters from Phenols.** By R. MELDOLA (*Chem. News*, 42, 39).—When nitroso-dimethylaniline acts on phenols (not containing the methyl-group) the oxygen of the nitroso-group directly attacks the hydrogen of the aromatic nucleus, thus:



The compounds formed are crystalline violet colouring matters, forming readily oxidisable leuco-bases. O. N. Witt (this Journal, 35, 356) describes the action of nitroso-dimethylaniline on meta-toluenediamine, in which the oxygen of the nitroso-group attacks the hydrogen of the alcohol radical—



L. T. O'S.

**Amarine.** By A. CLAUS and K. ELBS (*Ber.*, 13, 1418—1421).—An ethereal solution containing amarine and methyl iodide in their

molecular proportions, deposits in the course of a few days crystals of amarine methiodide.

Amarine benzochloride can be obtained by a similar reaction. These bodies are soluble in hot alcohol; they are not attacked by ammonia, but are converted by alcoholic potash into methylamarine (m. p. 175°) and benzylamarine respectively.

*Methylamarine methiodide*, formed by the action of methyl iodide on a boiling alcoholic solution of amarine, crystallises in brilliant pyramids (m. p. 246°), which are soluble in alcohol. This substance is not acted on by ammonia, but is decomposed by alcoholic potash, forming *dimethylamarine*, a base crystallising in monoclinic prisms (m. p. 146°). The salts of dimethylamarine are, with the exception of the acetate, sparingly soluble in water. The iodide obtained by the union of hydriodic acid with the base is not identical with methylamarine methiodide, since it is readily decomposed by ammonia. By boiling an alcoholic solution of dimethylamarine with benzyl chloride, the chlorides of two new bases are obtained. The chlorides can be separated by the difference of their solubility in water. The sparingly soluble chloride yields a crystalline base, which melts at 204°; the soluble chloride gives a base, which melts at 158°.

Analogous results are obtained if ethyl bromide is substituted for benzyl chloride.

*Benzylamarine benzyl chloride* is soluble in alcohol; it begins to melt at 40°, and is completely liquefied at 75°. It is not attacked by ammonia, but is converted by alcoholic potash into *dibenzylamarine*. This base is deposited from its alcoholic solution in white needles (m. p. 146°). The hydrochloride of dibenzylamarine is quite distinct from benzylamarine benzyl chloride, since it is readily decomposed by ammonia.

W. C. W.

**Paraethylmethylphenol.** By G. MAZZARA (*Gazzetta*, 10, 256—257).—Paraethyltoluene (b. p. 162°), prepared by the action of sodium on a mixture of ethyl iodide and pure parabromtoluene, was converted into the sulphonic acid by heating it on the water-bath for several hours with twice its weight of a mixture of ordinary and fuming sulphuric acid. The barium salt obtained from the crude acid was converted into the potassium salt, and then fused with twice its weight of potash. The phenol extracted from the product in the usual way by acidifying with hydrochloric acid and agitating with ether, boiled constantly at 215° after rectification. Pure paraethylmethylphenol,  $C_6H_3MeEt.OH$ , is a colourless oil which does not solidify in a freezing mixture of ice and salt; is but sparingly soluble in water, and gives a blue colour with ferric chloride.

C. E. G.

**Cumophenols.** By P. SPICA (*Gazzetta*, 10, 246—253).—This paper contains further researches on the phenols obtained from the two cumenesulphonic acids, produced by the action of sulphuric acid on cumene (this vol., 166). When the crystalline para-cumophenol is gently heated with monochloroacetic acid,—soda-solution being added from time to time,—and the product decomposed by hydrochloric acid, an acid is produced, which may be purified by crystallisation first from

alcohol, and then from water. It forms long silky needles (m. p.  $81^{\circ}$ ), having the composition of cumophenolglycollic acid—



The *barium salt*,  $(\text{C}_{11}\text{H}_{13}\text{O}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , crystallises with difficulty in long prisms. The *lead salt*,  $(\text{C}_{11}\text{H}_{13}\text{O}_3)_2\text{Pb} + 2\text{H}_2\text{O}$ , forms micaceous scales, only sparingly soluble in cold, but readily in hot water or boiling alcohol. The *silver salt*,  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{Ag}$ , is obtained as a white flocculent precipitate, on adding silver nitrate to an aqueous solution of the acid which has been partially neutralised with ammonia; under the microscope, it is seen to consist of slender needles.

The liquid orthocumophenol, which boils at  $213\text{--}215^{\circ}$ , and not at  $218^{\circ}$  as previously stated, yields an oily acid when treated with monochloroacetic acid in the manner above described. It was converted into a barium salt, and the barium salt analysed, but the results obtained did not correspond with those required by a cumophenolglycollic acid.

The reactions of the two acids with various reagents is given in a tabular form.

C. E. G.

**A New Cumophenol.** By M. FILETTI (*Gazzetta*, 10, 279—280).—This is a preliminary notice on a new cumophenol, prepared by the action of nitrous acid on the cumidine from amidocumic acid. It boils at about  $214^{\circ}$ , under a pressure of 753 mm., and solidifies to a crystalline mass (m. p.  $8\text{--}10^{\circ}$ ) at a low temperature. Its methyl ether boils at  $198\text{--}199^{\circ}$  under a pressure of 751 mm. This would seem to be the third of the possible cumophenols, the (1 : 4), and (1 : 2) compounds having been previously described by Paternò and Spica and by Spica.

The author also notices that when amidocumic acid is distilled with baryta, besides cumidine, a small quantity of a white crystalline substance (m. p.  $88\text{--}89^{\circ}$ ) is formed. It is insoluble in acids, and contains nitrogen.

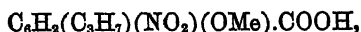
C. E. G.

**Derivatives of Natural and Synthetical Thymol.** By E. PATERNÒ and F. CANZONERI (*Gazzetta*, 10, 233—239).—In a former paper (this vol., p. 246), the authors discussed the action of dilute nitric acid on the ethers of thymol and camphothymol (carvacrol), the former yielding methoxynitrotoluic acid and ethoxynitrotoluic acid; whilst the synthetical camphothymol gave methoxy- and ethoxy-terephthalic acids. In order to elucidate this reaction more fully, the authors have studied the action of dilute nitric acid on the methyl ethers of the two nitrothymols.

*Action of Nitric Acid on the Methyl Ether of Nitrothymol.*—The nitrothymol was prepared by oxidising nitrosothymol with potassium ferricyanide, and after recrystallisation from dilute alcohol, it melted at  $138\text{--}139^{\circ}$ . It was converted into the methyl ether by digestion with methyl iodide, and a solution of potash in methyl alcohol; the crude product obtained by precipitation with water was then boiled with dilute nitric acid (1 acid to 4 of water) for five days. The crystalline precipitate after purification melted at  $175^{\circ}$ , and was shown to

be methoxynitrotoluic acid,  $C_6H_2Me(NO_2)(OMe).COOH$ , by the results of the analyses of the acid and of its barium salt. This confirms the authors' opinion that in the action of dilute nitric acid on the ethers of thymol, a nitro-derivative is first produced which is then oxidised to the nitrotoluic acid.

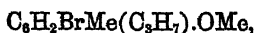
*Action of Nitric Acid on the Methyl Ether of Nitrocarvacrol.*—The nitro-derivative was prepared in a manner similar to that above described, but the yield was considerably smaller, much resinous matter being formed. The product obtained by boiling the nitrothymol with dilute nitric acid crystallised in small prismatic needles (m. p. 145–146°), easily soluble in alcohol, ether, benzene, and chloroform. On analysis it was found to be *methoxypropylnitrobenzoic acid*—



which was confirmed by an analysis of the barium salt; the latter forms fine lustrous prisms of a pale yellow colour.

The authors consider that the difference in behaviour of the two nitrothymol derivatives is due to the different relative positions of the  $NO_2$  and  $C_3H_7$  groups.

The methyl ether of thymol was submitted to the action of bromine, by passing air saturated with its vapour over the ether in the proportions of 2 Br to 1 mol. of the ether, and the product, after being washed with water and potash solution, was fractionally distilled, when the greater portion passed over between 263° and 265°. On analysis, however, it was found to contain somewhat more bromine than that required by the formula of the monobromo-derivative, so that it probably consisted of the *methyl ether of monobromothymol*—



mixed with a small portion of the dibromo-derivative. When submitted to the oxidising action of dilute nitric acid, it yielded a product which was separated by fractional crystallisation into various portions melting at different temperatures from 140° to 245°. The fraction melting at 193–194° had the composition of *methoxydibromotoluic acid*,  $C_6HBr_2Me(OMe).COOH$ ; it crystallises from benzene in transparent needles, and from dilute alcohol in silky scales. It is very soluble in ether or alcohol, but almost insoluble in water. The fractions more soluble in water seemed to contain methoxynitrotoluic acid.

It is possible to explain the formation of these two acids on the supposition that in the monobromo-derivative the bromine has entered by substitution into the  $C_3H_7$  group. Under these circumstances, a portion of the compound might be converted into methoxynitrotoluic acid, whilst the bromine, liberated by the oxidation of the  $C_3H_6Br$  group, would enter into the reaction to give rise to the dibrominated derivative.

C. E. G.

**Amidophenyl Mercaptans or Thiohydranilines.** By A. W. HOFMANN (*Ber.*, 13, 1223–1240).—This consists of a continuation of the investigation, some account of which has already appeared (this vol., 386–387). In a foot-note the author states that 1 part of

sulphur and 3 parts of phenylbenzamide give the best yield of benzenylamidophenyl mercaptan, and that by action of concentrated nitric and sulphuric acids this body is converted into a mononitro-derivative (m. p. 188°), which yields an amido-derivative on reduction.

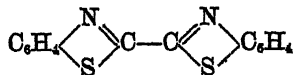
*Methenylamidophenyl mercaptan* may be obtained by heating form-anilide with sulphur, thus:  $C_6H_5.NH.CHO + S = C_6H_5 \begin{smallmatrix} \diagup N \\ \diagdown S \end{smallmatrix} CH +$

$H_2O$ . This represents but a small portion of the decomposition, some of the formanilide yielding aniline and carbonic oxide (this Journal [2], 1, 72); further, sulphuretted hydrogen and thioanilide are formed.

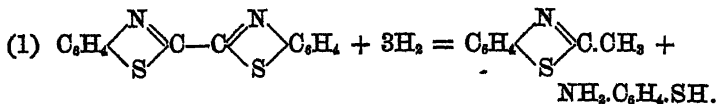
*Ethenyl-, propionyl-, and pentenyl-amidophenyl mercaptans* are obtained by the action of sulphur at high temperatures on the anilides of acetic, propionic, and valerianic acids. The yield of these bases is comparatively small, other reactions taking place.

*Benzenylamidophenyl mercaptan* is also obtained in small quantities by heating phenylacetanilide with sulphur. Phenylacetanilide is obtained by boiling aniline with phenylacetic acid. It crystallises in shining flat needles (m. p. 117°).

*Oxalic acid Derivative of Amidophenyl Mercaptan*,  $C_{14}H_8N_2S_2$ .—When acetanilide is heated to boiling with sulphur for some time, sulphuretted hydrogen and carbonic anhydride are formed, and acetic acid, acetanilide, aniline, and the above ethenyl-base distil over. The evolution of sulphuretted hydrogen diminishes after some time, and a sublimate is formed in the retort. If the crystalline residue in the retort, after extraction with alcohol to remove aniline, &c., be sublimed in a current of air, the oxalic acid derivative of amidophenyl mercaptan is obtained in large yellow needles. It is insoluble in the ordinary solvents. It crystallises from hot toluene in microscopic prisms. It is very sparingly soluble in hot alcohol, and its alcoholic solutions have a bitter taste. It melts at about 300°, and may be distilled without decomposition. That its constitution is



is shown by its being resolved into amidophenyl mercaptan and oxalic acid by heating with potash at 200°; and further, its decomposition into ethenylamidophenyl mercaptan and aniline sulphhydrate by hydriodic acid and phosphorus at 150°, thus—



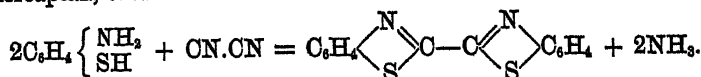
That the above is the constitution of this compound is further shown by its production in the following cases:—

(1.) When oxalic acid and amidophenyl mercaptan react in presence of phosphorous trichloride.

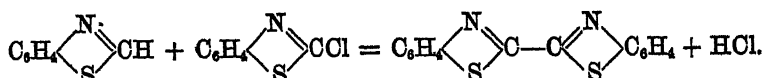


(2.) By the action of amidophenyl mercaptan on crystalline ethyl oxalate.

(3.) By passing cyanogen into an alcoholic solution of amidophenyl mercaptan, thus—



(4.) By the action of the methenyl base on its chloro-derivative, thus—



(5.) By the action of zinc on the chloromethenyl base.

Finally it is obtained by acting on the methenyl base with acetic chloride or benzoic chloride in sealed tubes at 150°.

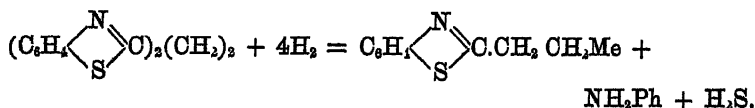
A partial explanation of its formation from acetanilide is obtained by supposing that a thioacetanilide,  $\text{S}(\text{C}_6\text{H}_4.\text{NH}\text{Ac})_2$  or  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ , is first formed, and this when decomposed by sulphur gives the following products:—



As a means of preparing orthamidophenyl mercaptan, the author recommends the preparation of this oxalic acid derivative from acetanilide, and its decomposition with potash at 200°.

*Derivatives of Amidophenyl Mercaptan.*—(1.) *Succinyl* derivative,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_2$ , is obtained by action of the mercaptan on succinamide; the latter is dissolved with liberation of ammonia. It crystallises from alcohol in beautiful colourless needles (m. p. 137°). It forms a hydrochloride crystallising in lemon-yellow needles, which are decomposed by water. The platinochloride forms sparingly soluble crystalline scales. The aurochloride,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_2.\text{HCl}.\text{AuCl}_3$ , crystallises in yellow needles.

Potash resolves this succinyl derivative into amidophenyl mercaptan and succinic acid; phosphorus and hydriodic acid resolve it apparently into the tetrenyl base and aniline, thus—

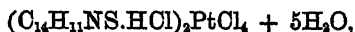


(2.) The *phthalyl* derivative,  $(\text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{N} \\ \text{S}\end{array}\right\rangle\text{O})_2$  :  $\text{C}_6\text{H}_4$ , is obtained by

the action of phthalic anhydride or chloride on amidophenyl mercaptan. It crystallises from concentrated alcoholic solutions in thick prisms, and from dilute in fine needles. It is soluble in ether, but insoluble in water, and melts at 112°. It is a feeble base. Its hydrochloride and platinochloride are both decomposed by water.

(3.) *Glycollyl* derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{OH}$ , is obtained from amidophenyl mercaptan and chloracetic acid. It crystallises from hot alcohol in long fine brittle needles (m. p.  $176^\circ$ ). It is insoluble in water and hydrochloric acid, but dissolves in concentrated sulphuric acid, and is reprecipitated from this solution by water. The influence of the hydroxyl group is shown by its solubility in alkalis, from which solutions it is reprecipitated by acids.

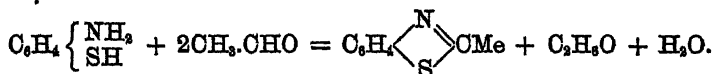
(4.) *Phenylacetic* derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{Ph}$ . Its hydrochloride is obtained by acting on amidophenyl mercaptan with phenylacetic chloride. This salt crystallises from hydrochloric acid in light yellow, stellate, grouped needles. It is easily decomposed by water or alkalis, yielding the base as an oily liquid, insoluble in water, but soluble in alcohol and ether. The platinochloride,



crystallises in yellow needles.

(5.) The *Cinnamyl* derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CH} : \text{CHPh}$ , is obtained by heating cinnamic acid with amidophenyl mercaptan. It crystallises from alcohol in thick strongly refractive prisms, melting at  $115^\circ$ . It is a feeble base; forms a hydrochloride and platinochloride. Similarly to the above derivative, it is resolved by potash into the mercaptan and cinnamic acid.

Amidophenyl mercaptan reacts with aldehydes, yielding interesting results; e.g., with acetaldehyde the ethenyl base has been obtained, thus—

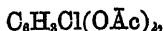


Benzaldehyde yields the benzenyl base, and salicylaldehyde yields a salicyl derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ . This compound crystallises from alcohol in beautiful shining needles (m. p.  $129^\circ$ ). It forms salts with acids, and is also soluble in alkalis, owing to the presence of the phenol group. Potash resolves it into the mercaptan and salicylic acid. This compound has been obtained by Schuhwirth by the action of sulphur on phenylsalicylamide.

Amidophenyl mercaptan reacts with hydrocyanic acid, yielding methenylamidophenyl mercaptan, and similarly with acetonitril and benzonitril it yields the ethenyl and benzenyl base respectively, the reaction in the last two cases requiring a higher temperature than in the first.

P. P. B.

**Chlorinated Quinones.** By S. LEVY and G. SCHULTZ (*Ber.*, 13, 1427—1430).—*Monochloroquinol* forms a diacetic compound,



which crystallises in transparent prisms (m. p.  $72^\circ$ ). The dibenzoic derivative,  $\text{C}_6\text{H}_5\text{Cl}(\text{OBz})_2$ , crystallises in long needles (m. p.  $130^\circ$ ), soluble in xylene, ether, benzene, chloroform, hot alcohol, and strong sulphuric acid. Heated with phthalic anhydride and strong sulphuric acid, monochloroquinol yields a chlorinated quinizarine, which dissolves in a solution of soda with a blue colour. An aqueous solution of monochloroquinol is converted by oxidation with chromic acid into monochloroquinone and a small quantity of  $\alpha$ -dichloroquinone. The *monochloroquinone*, after repeated recrystallisation from alcohol, forms thick rhombic prisms of a yellow colour, which melt at  $57^\circ$ . It dissolves in concentrated hydrochloric acid, forming a mixture of  $\alpha$ -di- and tri-chloroquinols. The former compound (m. p.  $164^\circ$ ) yields on oxidation  $\alpha$ -dichloroquinone (m. p.  $154^\circ$ ), which is converted by strong hydrochloric acid into a mixture of trichloroquinol,  $\text{C}_6\text{HCl}_3(\text{OH})_2$ , and tetrachloroquinol.

When  $\beta$ -dichloroquinone (prepared by the action of nitric acid on trichlorophenol) is treated with strong hydrochloric acid, the same results are obtained. From neither  $\alpha$ - nor  $\beta$ -dichloroquinone can a chlorinated quinizarine be derived. The benzoic derivative of trichloroquinol crystallises in colourless needles (m. p.  $174^\circ$ ), sparingly soluble in cold alcohol.

*Trichloroquinone* is changed into *tetrachloroquinol* by boiling with strong hydrochloric acid. This substance forms a benzoic derivative (m. p.  $230^\circ$ ), which is sparingly soluble in alcohol and freely soluble in benzene.

*Tetrachloroquinone*,  $\text{C}_6\text{Cl}_4\text{O}_2$ , forms yellow plates belonging to the monoclinic system. The reduction of tetrachloroquinone by strong hydrochloric acid to tetrachloroquinol shows that intermediate products of the composition  $\text{C}_6\text{Cl}_4(\text{OCl})(\text{OH})$  do not exist.

The preceding experiments show that, starting from monochloroquinol, it is possible to proceed step by step to the formation of tetrachloroquinol.

W. C. W.

**Thymoglycollic Acids.** By P. SPICA (*Gazzetta*, 10, 340—349).—In this paper two thymoglycollic acids are described, obtained from natural thymol and camphothymol (carvacrol) respectively.

The derivative from natural thymol was prepared by fusing a mixture of 12 parts of thymol with 7.5 of monochloroacetic acid, and then gradually adding the mixture to 50 of soda solution of sp. gr. 1.35. The product forms two layers, which mix on adding an equal volume of water: the unaltered thymol is removed by adding a slight excess of hydrochloric acid, neutralising with ammonium carbonate, and agitating several times with ether. The thymoglycollic acid is then precipitated by an acid, and purified by crystallisation from dilute alcohol. The yield is theoretical for the amount of thymol acted on. Pure thymoglycollic acid,  $\text{C}_6\text{H}_3\text{Me}(\text{C}_6\text{H}_7)\text{O}.\text{CH}_2.\text{COOH}$ , forms fine prisms (m. p.  $147$ — $148^\circ$ ), sparingly soluble in water, but easily in

alcohol or ether. The *barium salt*,  $(C_{12}H_{16}O_3)_2Ba \cdot 2H_2O$ , crystallises with difficulty; it loses the  $2H_2O$  at  $120-130^\circ$ . The *lead salt*,  $(C_{12}H_{16}O_3)_2Pb$ , is obtained as a white amorphous precipitate on adding lead acetate to a solution of the acid previously neutralised with ammonia. The *silver salt*,  $C_{12}H_{16}O_3Ag$ , forms microscopic prisms, almost insoluble in boiling water. *Ethyl thymoglycollate*,  $C_{12}H_{18}O_5Et$ , prepared by saturating an alcoholic solution of the acid with dry hydrochloric acid, is a limpid, almost colourless liquid (b. p.  $290^\circ$ ), having an odour resembling that of ethyl oxalate. It does not solidify in a mixture of ice and salt, but when allowed to stand some days it deposits a colourless substance (m. p.  $110^\circ$ ), possibly a polymeric modification of the ether. When treated with aqueous ammonia, the ethyl salt yields *thymoglycollamide*, a substance crystallising in prisms (m. p.  $96-97^\circ$ ), sparingly soluble in cold water, but readily in hot.

Camphothymol (carvacrol, b. p.  $233-235^\circ$ ) when treated with monochloroacetic acid and soda in the manner above described, yielded a mixture of three acids; one, melting at about  $110^\circ$ , formed but in very minute quantity, another, melting at  $126-127^\circ$ , and a third, *carvacrolglycollic acid*; this is the principal product of the reaction, the others owing their origin to impurities in the carvacrol employed, or to a secondary action. These acids were first separated by fractional crystallisation, and the carvacrolglycollic acid was finally purified by converting it into the barium salt and repeatedly crystallising the latter. Pure carvacrolglycollic acid crystallises in colourless needles (m. p.  $149^\circ$ ), very sparingly soluble in cold water, but readily in alcohol or ether. The *barium salt*,  $(C_{12}H_{16}O_3)_2Ba + 4H_2O$ , is more soluble in hot water than in cold. The *lead salt*,  $(C_{12}H_{16}O_3)_2Pb$  is thrown down as a gummy precipitate, but crystallises from alcohol in tufts of microscopic needles. The *silver salt*,  $C_{12}H_{16}O_3Ag$ , forms microscopic needles. *Ethyl carvacrolglycollate* is an oil (b. p.  $289^\circ$ ), which solidifies at a low temperature. The *amide*, which closely resembles its isomeride, melts at  $67-68^\circ$ .

The acid of melting point  $126-127^\circ$  forms crystalline nodules built up of microscopic needles. It is more soluble in water than the carvacrolglycollic acid, and is also distinguished from the latter inasmuch as it gives an orange-yellow precipitate with ferric chloride, whilst carvacrolglycollic acid solution merely becomes turbid. The silver salt is amorphous, and the results of its analysis, as well as of that of the acid itself, corresponds with a thymolcarboxylic acid.

The author draws attention to the fact that although the fusion points of the two isomeric glycollic acids, and also the boiling points of their ethereal salts, are very close, there is a difference of about  $30^\circ$  in the melting points of the amides. C. E. G.

**Constitution of  $\alpha$ -Toluenedisulphonic Acid.** By P. CLASSÉN and H. BERG (*Ber.*, 13, 1170-1171).—The constitution of  $\alpha$ -toluenedisulphonic acid, which has been investigated by Blomstrand (*Ber.*, 4, 717) and Hakansson (*Ber.*, 5, 1084), is shown to be orthoparatoluenedisulphonic acid, since it is formed both from para- and from orthotoluenedisulphonic acid by the action of fuming sulphuric acid.

P. P. B.

**Cyrenesulphonic Acids.** By P. SPICA (*Gazzetta*, 10, 254—255).—This is mainly a claim of priority in respect of a paper by Claus (*Ber.*, 13, 901).—The author has repeated his former experiments (*Gaz.* 9, 397) on the action of sulphuric acid on cyrene, and finds that two sulphonic acids are really produced, the barium salts of which crystallise with  $3\text{H}_2\text{O}$  and  $4\text{H}_2\text{O}$  respectively. The sulphonic chlorides have also been prepared, as well as the amides. In conclusion, the author observes, "As is usual in Germany, Claus makes no mention of the researches on cyrene published in Italy."

C. E. G.

**Nitro-derivatives of Diphenyl-mono- and Di-sulphonic Acids.** By S. GABRIEL and A. K. DAMBERGIS (*Ber.*, 13, 1408—1412).—*Copper nitrodiphenylsulphonate* is prepared by pouring a solution of paranitrodiphenyl in warm strong sulphuric acid into cold water, and adding copper sulphate to the mixture. The copper salt is deposited in small rhombohedral crystals, which have the composition  $[\text{C}_{12}\text{H}_8(\text{NO}_2)\text{SO}_3]_2\text{Cu} + 4\text{H}_2\text{O}$ .

*Sodium nitrodiphenylsulphonate*,  $\text{C}_{12}\text{H}_8(\text{NO}_2)\cdot\text{SO}_3\text{Na}$ , is obtained in anhydrous lustrous plates by boiling the copper salt with soda. The *barium salt* forms glistening white needles, containing 4 molecules of water.

*Nitrodiphenylsulphonic chloride*,  $\text{C}_{12}\text{H}_8(\text{NO}_2)\cdot\text{SO}_2\text{Cl}$ , is deposited from a glacial acetic acid solution in needles (m. p.  $178^\circ$ ). It can be prepared by the action of phosphorus pentachloride on the sodium salt, or more readily by dissolving diphenylmonosulphonic chloride in fuming nitric acid. The formation of the chloride by these two methods indicates that the sulphonic acid is a dipara-derivative, viz., paranitrodiphenylparasulphonic acid.

*Nitrodiphenylsulphamide*, prepared by digesting the chloride with alcoholic ammonia, melts at  $228^\circ$ .

*Paramidodiphenyl-parasulphhydrate hydrochloride*,



is formed when hydrochloric acid is added to the solution in soda of the yellow precipitate produced by the addition of water to the product of the action of tin and hydrochloric acid on the nitrosulphonic chloride. It crystallises in lustrous plates, which are decomposed by water, forming an amorphous mass. On the addition of potassium monochloracetate to a solution of the hydrochloride in an alkali, potassium amidodiphenylthiacetate is precipitated. The free acid forms granular or tabular crystals, which dissolve sparingly in water, and melt above  $200^\circ$ .

Nitro-derivatives of diphenyldisulphonic chloride are obtained by adding 10 parts of strong sulphuric acid to a solution of 1 part of the sulphonic chloride in 10 parts of fuming nitric acid. If the temperature is not allowed to reach  $60^\circ$ , the only mononitro-derivative (m. p.  $130^\circ$ ) is formed; if the mixture is heated at  $90$ — $95^\circ$ , the dinitro-product (m. p.  $166^\circ$ ) is obtained. The solution is poured into water, and the precipitate dried and recrystallised from glacial acetic acid.

The crystalline double salt, which is formed by the reduction of the mononitro-derivative with tin and hydrochloric acid, is decomposed

by boiling water with the production of *amido-diphenyl disulphhydrate*,  $\text{HS.C}_6\text{H}_4.\text{C}_6\text{H}_5.(\text{NH}_2).\text{SH}$  (m. p.  $153^\circ$ ). W. C. W.

**Phenanthrene Derivatives.** By R. ANSCHÜTZ and I. v. SIEMENSKI (*Ber.*, 13, 1179—1180).—When bromophenanthrene is heated on the water-bath with strong sulphuric acid, a bromosulphonic acid is obtained, which is soluble in water. On adding potash, *potassium bromophenanthrenemonosulphonate*,  $\text{C}_{14}\text{H}_9\text{Br}.\text{SO}_3\text{K}$ , separates as a white precipitate; it crystallises from hot water in small white needles. Fusion with potash yields no hydroxyl compound.

*Silver bromophenanthrenemonosulphonate*,  $\text{C}_{14}\text{H}_9\text{Br}.\text{SO}_3\text{Ag}$ , is obtained by adding silver nitrate to a hot aqueous solution of the potassium compound. On cooling, it separates out in greyish-white shining needles. These derivatives are decomposed by strong nitric acid with great difficulty.

*Barium bromophenanthrenemonosulphonate*,  $(\text{C}_{14}\text{H}_9\text{Br}.\text{SO}_3)_2\text{Ba}$ , forms a white amorphous precipitate, insoluble in water. The free acid is obtained with difficulty in a pure state; other isomerides are simultaneously formed.

From the diazo-compound of sulphanilic acid and phenanthrol (Rehs, this Journal, 34, 76), a red colouring matter belonging to the tropaeoline

class has been obtained. Further phenanthrenequinone,  $\begin{array}{c} \text{C}_6\text{H}_3(\text{OH})\text{CO} \\ | \\ \text{C}_6\text{H}_4\text{—CO} \end{array}$ ,

obtained from phenanthrol, has marked colouring properties. It is soluble in a hot solution of sodium hydrogen sulphite, from which acids precipitate it as a red amorphous powder. Alkalis dissolve it, forming carmine-red solutions; heated above  $200^\circ$ , it decomposes partially, but may be sublimed, and is obtained in the form of red needles resembling alizarin. P. P. B.


**Bromonitro-, Nitro-, and Amido-camphor.** By R. SCHIFF (*Ber.*, 13, 1402—1406; also *Gazzetta*, 10, 317 and 362).—*Bromonitro-camphor*,  $\text{C}_{10}\text{H}_{14}\text{BrNO}_2$ , is formed together with camphoric acid by heating bromo-camphor with nitric acid for several hours. It is a white crystalline body (m. p.  $105^\circ$ ), almost insoluble in cold alcohol. If the preceding compound is dissolved in alcoholic potash, the alcohol removed by evaporation, and dilute sulphuric acid added to the aqueous solution of the residue, *nitro-camphor*,  $\text{C}_{10}\text{H}_{14}(\text{OH})\text{NO}_2$ , separates as an oily liquid, which slowly solidifies. The crude product can be purified by solution in ammonia and reprecipitation by acids. The pure substance melts at  $83^\circ$ ; its aqueous solution is coloured red by ferric chloride, and forms a crystalline nitroso-derivative with potassium nitrite. Nitro-camphor is converted into camphoric acid by nitric acid, and into camphoric anhydride by nitrosulphuric acid. Heated in a current of steam, in the absence of air, it is decomposed, yielding camphoric acid, camphoric anhydride, and ammonia. Nitro-camphor can also be prepared by the action of zinc and dilute sulphuric acid on an ethereal solution of bromonitro-camphor.

When a solution of nitro-camphor in potash is treated with sodium amalgam, *amido-camphor*,  $\text{C}_{10}\text{H}_{14}(\text{OH}).\text{NH}_2$ , is formed. This powerful

base distils without decomposition at  $246.4^{\circ}$ , and solidifies on cooling to a wax-like mass. It forms a hydrochloride, crystallising in needles, and a crystalline platinochloride  $(C_{10}H_{17}NO \cdot HCl)_2PtCl_4$ , which is soluble in hot alcohol. The aqueous solution reduces metallic salts, and resembles hydroxylamine in many of its reactions.

A crystalline oxycamphor (m. p.  $155^{\circ}$ ) is formed when the aqueous solution is treated with nitrous acid. It is volatile in a current of steam, and is soluble in alkalis.

Amido-camphor hydrochloride is decomposed by distillation in a current of steam into *dicamphorilimide*,  $C_{20}H_{31}NO_2$ , which is found in the distillate, and *camphimide*, which is contained in the residue. The former of these compounds crystallises in yellow needles (m. p.  $160^{\circ}$ ), which are insoluble in acids: on adding potash to the residue camphimide is obtained as an oily liquid, which rapidly solidifies.

This base appears to have the constitution  $C_9H_{14}$   NH.

W. C. W.

**Constitution of Bromo-camphor.** By R. SCHIFF (*Ber.*, 13, 1406—1407; also *Gazzetta*, 10, 332).—The conversion of bromo-camphor into camphor and of nitrobromo-camphor into nitro-camphor by the action of nascent hydrogen or of alcoholic potash, seems to indicate that bromo-camphor contains the group  $\equiv OBr$ .

The formation of sodium camphor, when a solution of bromo-camphor in toluene is treated with metallic sodium, is also evidence in favour of this view.

Sodium camphor is converted into ordinary camphor by the action of water.

W. C. W.

**Action of Zinc Chloride on Bromo-camphor.** By R. SCHIFF (*Ber.*, 13, 1407—1408; also *Gazzetta*, 10, 317).—By heating a mixture of zinc chloride and bromo-camphor at  $150$ — $160^{\circ}$  until the evolution of hydrobromic acid ceases and then distilling the residue, *hexhydro-paraxylene*,  $C_8H_{16}$ , and liquid thymol,  $C_{10}H_{16}O$ , are obtained.

Hexhydroxylene boils at  $187.6^{\circ}$  (corr.), and has the sp. gr. 0.7956 at  $4^{\circ}$ . The trinitroparaxylene derived from it melts at  $127^{\circ}$ .

The thymol (sp. gr. 1.0101 at  $4^{\circ}$ , b. p.  $232^{\circ}$ ) appears to be identical with the thymol Kekulé (*Ber.*, 6, 934) obtained by the action of iodine on camphor.

W. C. W.

**Camphocarbonic Acid.** By J. KACHLER and F. V. SPITZER (*Ber.*, 13, 1412—1413).—*Camphocarboxylic acid*,  $C_{11}H_{16}O_3$ , is deposited on recrystallisation from warm water in colourless needles, which melt at  $124^{\circ}$ , but begin to decompose below  $100^{\circ}$ . By treating the ethereal solution of the acid with metallic sodium, a non-hygroscopic sodium compound,  $C_{22}H_{31}NaO_6$ , is produced, from which the corresponding barium salt,  $C_{22}H_{30}BaO_6$ , can be prepared.

By the action of phosphorus pentachloride on camphocarboxylic acid, a chloride crystallising in prisms (m. p.  $44^{\circ}$ ) is obtained. A crystalline compound is also formed by treating a solution of the acid in chloroform with phosphoric anhydride.

W. C. W.

**Preparation of Camphoric Acid and Camphoric Anhydride.** By P. MAISSEN (*Gazzetta*, 10, 280—281).—Instead of acting directly on camphor with nitric acid, the mixture of camphor and borneol obtained as a residue in preparing borneol by Baubigny's method may be employed. Camphor is dissolved in any convenient hydrocarbon boiling above  $100^{\circ}$ , and sodium is introduced into the hot solution in small pieces at a time, until it no longer dissolves. When cold, the pasty mass is agitated with water, and the oily layer separated and distilled. The residue in the retort may be used for the preparation of camphoric acid. For this purpose, 300 grams are boiled with 800 of nitric acid and 200 of water for three days. The crude acid which separates in the crystalline state may be purified by dissolving it in potash, filtering, and precipitating with an acid. The yield is about 80 per cent., whilst camphor never gives more than 50 per cent. of its weight.

To prepare camphoric anhydride, the camphoric acid is boiled with acetic anhydride and dry sodium acetate in molecular proportions. When cold, the product is extracted with cold water, and the residue crystallised from boiling alcohol. In this way, almost the whole of the camphoric acid is obtained as pure anhydride (m. p.  $217^{\circ}$ ).

C. E. G.

**Products of the Distillation of Colophony.** By A. RENARD (*Compt. rend.*, 91, 419—421).—By subjecting colophony to several fractional distillations, and removing acids from the distillates by washing them with alkalis, a hydrocarbon (b. p.  $103-106^{\circ}$ ) is obtained, for which the author suggests the name *heptene*. It is purified by washing with caustic soda, drying first over calcium chloride, and then over sodium, and finally distilling over sodium in a current of carbonic anhydride. Its analysis and vapour-density correspond with the formula  $C_7H_{12}$ . It is a mobile colourless liquid, soluble in alcohol and ether, sp. gr. =  $0.8031$  at  $20^{\circ}$ ; it has a peculiar odour, and is without action on polarised light. It absorbs oxygen from the air, evolving carbonic anhydride.

When treated with chlorine, it forms a resinous mass, with evolution of hydrochloric acid. Bromine acts on the hydrocarbon with great violence. If however, it is dropped slowly into the cooled hydrocarbon, and the mixture containing excess of bromine be allowed to stand in the shade for two or three days, a thick liquid is obtained, which, after washing with alkalis, yields a yellow oil. By extracting the oil with ether and allowing the ethereal solution to stand, crystals of a hexa-bromo-compound,  $C_7H_2Br_6$ , separate out (m. p.  $134^{\circ}$ ); it decomposes at  $150^{\circ}$ .

By allowing the above mixture of hydrocarbon and bromine to stand for 8—10 days in the sunlight, an isomeride of the above compound is obtained; a thick, oily brown liquid, decomposing at  $150^{\circ}$ .

A dibromide,  $C_7H_{12}Br_2$ , is obtained by dropping a solution of the hydrocarbon in ether into a cooled solution of bromine in ether, keeping the bromine in excess. On allowing the solution to evaporate spontaneously, white crystals are formed, which are very unstable, decomposing a few minutes after their formation.

Nitric acid (sp. gr.  $1.15$ ) acts on the heptene at  $80^{\circ}$ , forming acetic,



formic, oxalic, and succinic acids, with evolution of carbonic oxide and carbonic anhydride. Fuming nitric acid acts with great violence on the hydrocarbon. Gaseous hydrochloric acid forms a green liquid with heptene, but no hydrochloride is formed. An aqueous solution of the gas is without action.

By treating the cooled hydrocarbon with concentrated or fuming sulphuric acid, an oily liquid is obtained, consisting of a mixture of unaltered heptene and diheptene,  $C_{14}H_{28}$  (b. p. 235–240°). Diheptene is readily oxidised, absorbing oxygen eight or ten times more quickly than heptene. It has no action on polarised light. A sulphonic acid is also formed, which yields a very soluble barium salt.

Heptene unites with the elements of water, forming a crystalline hydrate.

L. T. O'S.

**Chlorophyll from Eucalyptus Globulus.** By E. SCHUNCK (*Chem. News.*, 31, 32).—The peculiar appearance presented by the leaves of the *Eucalyptus globulus* is due to an exceedingly thin covering of fatty matter, such as is seen on fresh plums and other fruit. The ethereal solution of this fat leaves a semicrystalline residue which melts much below 100°; it is partially soluble in alkalis, and, therefore, most probably contains some fatty acid. The ethereal or alcoholic extract of the leaves containing chlorophyll, when kept tightly corked and in the dark, assumes a yellowish tint, and shows absorption-bands corresponding with those of "acid chlorophyll." The extract of green grass does not behave in a similar manner, but, on exposure to the action of sunlight, it gradually loses its colour and becomes pale yellow. The alcoholic extract of eucalyptus leaves also becomes paler on exposure to light. The change which takes place is attributed to the action of the essential oil contained in the extract on the oxygen of the air forming ozone, which acts on the alcoholic extract of the chlorophyll. Extract of orange leaves when kept in the dark remains unchanged. After insolation, it slightly differed from an extract of grass made at the same time and exposed to sunlight along with it. The bands I and IVa absent in the grass-spectrum were present in that of the orange extract.

L. T. O'S.

**Crystallised Chlorophyll.** By HOPPE-SEYLER (*Bied. Centr.*, 1880, 375–376).—Leaves of grass after being treated with ether until the wax was completely removed, were boiled with alcohol, which dissolved two colouring matters; both of these crystallised out during cooling. The first is red in transmitted light, and is evidently identical with the substance to which Bougarel gives the name of erythrophyll. After this substance has been removed by filtration, the filtrate concentrated, and the residue washed repeatedly with water, dissolved in ether, and left to evaporate, reappear on the sides and bottom of the vessel; they are granular crystals, brown in transmitted, green in reflected light. These crystals may be purified by repeated washings in cold and solution in warm alcohol and in ether.

The author gives this substance the name of *chlorophyllan*; it has the consistence of soft wax; in a fairly dry condition, it melts at 110°. The crystals are sparingly soluble in cold alcohol, but dissolve readily

in ether or chloroform. The solution shows the fluorescence of alcoholic or ethereal extracts of green plants, and a similar but not precisely identical spectrum, which leads the author to the conclusion that chlorophyllan does not exist as such in the plant, but is formed during the treatment; the percentage composition is given as C, 73.4; H, 9.7; N, 5.62; O, 9.57; P, 1.37; Mg, 0.34; the phosphorus and magnesium are not considered as impurities, but appear to be normal constituents of the substance. Further experiments are promised.

J. F.

**Behaviour of the Cinchona Alkaloids with Potassium Permanganate.** By S. HOOGEWERFF and W. A. v. DOEP (*Liebig's Annalen*, 204, 84—118).—Quinine, cinchonine, quinidine, and cinchonidine, when oxidised by permanganate, yield tricarboxypyridinic acid together with ammonia, oxalic and carbonic acids, and some other products which need further examination. A dicarboxylic acid identical with Weidel's cinchomeronic acid is easily obtained from the tricarboxylic acid. A monocarboxylic acid has also been prepared but not fully investigated.

*Preparation of Tricarboxypyridinic Acid.*—The alkaloids or their sulphates are mixed with potash solution and heated to boiling in a flask in a calcium chloride bath. The permanganate is added in small quantities until the red colour imparted by it remains permanent after an hour's boiling.

After addition of nitric acid and concentration of the solution the potassium is removed by crystallisation as potassium nitrate. Barium nitrate is then added as long as a precipitate is formed. This precipitate, consisting of barium oxalate and tricarboxypyridinate, is decomposed by sulphuric acid.

Tricarboxypyridinic acid forms transparent tabular crystals, which appear greenish by reflected light, and exhibit a strong play of colours under polarisation. It is moderately soluble in alcohol and very sparingly so in ether and benzene, but dissolves readily in boiling water. It gives a faint red colour with ferrous salts. It gives up its water of crystallisation between 100° and 120° without decomposition, but becomes blackened at 190°, and melts at 244—250°. The aqueous solution gives an amorphous precipitate with barium acetate; with calcium acetate, a warty crystalline mass of needles; with silver nitrate, an amorphous precipitate which becomes crystalline after a time, and is not much altered by exposure to light; with copper acetate, a bright blue amorphous precipitate; with lead acetate (and also the basic acetate), white amorphous precipitates. No red fumes are evolved when the acid is boiled with concentrated nitric acid. It is readily acted on by permanganate in acid, but not in alkaline solutions. It consists in the anhydrous state of  $C_8H_5NO_6$ , and is tribasic. It crystallises from aqueous solutions with  $1\frac{1}{2}$  mol. of water. The neutral *potassium salt*,  $C_8H_4K_3NO_6 + 3H_2O$ , forms brilliant plates which exhibit a fine play of colour in polarised light. The neutral *barium salt* when prepared by addition of barium acetate to a solution neutralised with ammonia, consists (if precipitated in the cold) of  $C_8H_4Ba_3NO_6 + 8H_2O$ , and loses  $7H_2O$  at 100°, and all its water at 280—300°. If the barium acetate

is added to an acid solution, another salt containing, when dried in air, only  $6\text{H}_2\text{O}$  is obtained, in addition to the one just described. The *calcium salt* contains  $7\text{H}_2\text{O}$ . The *normal silver salt*  $\text{C}_8\text{H}_5\text{Ag}_3\text{NO}_6 + 2\text{H}_2\text{O}$ , consists of an amorphous precipitate which loses part of its water over sulphuric acid, and is not much altered by exposure to light. It is obtained by adding silver nitrate to a solution of the acid neutralised by ammonia. If the aqueous solution of the acid is mixed with silver nitrate, a precipitate is thrown down which is at first amorphous, afterwards crystalline, and which consists of  $\text{C}_8\text{H}_5\text{Ag}_3\text{NO}_6 + \text{H}_2\text{O}$ . Another silver salt,  $\text{C}_8\text{H}_4\text{AgNO}_6 + \text{C}_8\text{H}_5\text{NO}_6$ , crystallising with  $2\frac{1}{2}\text{H}_2\text{O}$ , may be obtained by dissolving the neutral silver salt in warm dilute nitric acid and concentrating the solution.

*Cinchomeric acid* may be obtained by heating tricarboxypyridinic acid to  $180\text{--}190^\circ$ , when decomposition takes place in accordance with the equation,  $\text{C}_8\text{H}_5\text{NO}_6 = \text{C}_7\text{H}_5\text{NO}_4 + \text{CO}_2$ . This acid is identical with the one Weidel and Schmidt (*Annalen*, 173, 96) obtained by direct oxidation of quinine, cinchonine, and cinchonidine. It is sparingly soluble in ordinary solvents. It gives no colour when mixed with ferrous sulphate. It contains no water of crystallisation, and melts at  $250^\circ$  with evolution of carbonic anhydride, but without being blackened. When distilled with excess of calcium hydrate, the distillate smells strongly of pyridine. The *normal barium salt*,  $\text{C}_7\text{H}_5\text{BaNO}_4$ , forms tufts of needles which are sparingly soluble. The *normal calcium salt* crystallises in large prisms, and is more easily soluble than the barium salt; when dried in air, it retains  $3\frac{1}{2}\text{H}_2\text{O}$ . The *normal silver salt*,  $\text{C}_7\text{H}_5\text{Ag}_3\text{NO}_6$ , is anhydrous, and not much altered by exposure to light. The *acid silver salt*,  $\text{C}_7\text{H}_4\text{AgNO}_6$ , is obtained by dissolving the acid in boiling water with addition of a few drops of nitric acid, and adding silver nitrate. It is crystalline and anhydrous. The *normal copper salt*,  $\text{C}_7\text{H}_5\text{CuNO}_4 + 4\text{H}_2\text{O}$ , forms dark blue sparingly soluble crystals. It loses its water of crystallisation at  $180^\circ$ .

Cinchomeric acid splits up on heating into pyrocinchomeric acid (*Ber.*, 13, 61) and nicotinic acid, whilst carbonic anhydride is evolved.

The action of permanganate on the four cinchona alkaloids seems to be as follows:—In the first stage, the molecules containing two nitrogen atoms are split into two groups containing one atom of nitrogen in each. In the second stage, the nitrogen of one of these groups is evolved as ammonia, while from the other several bodies containing nitrogen are obtained, among the rest, tricarboxypyridinic acid.

The authors do not agree with Weidel and Herzig's supposition that cinchomeric acid is constituted (according to Körner's pyridine and quinoline formula) as 1. 2. 3, the nitrogen having the place 1; but they assign this constitution to their quinolic acid obtained by the action of permanganate on quinoline, and which they consider to be the normal oxidation product of this body. (Compare *Jour. Chem. Soc., Trans.*, 1878, 102, and 1879, 189). G. T. A.

**Bromine Derivatives of Nicotine.** By R. LAIBLIN (*Ber.*, 13, 1212—1214).—By the action of bromine and water on nicotine in sealed tubes at 120—150°, the author has obtained a crystalline compound similar to that obtained by Cahours and Etard, which is probably  $C_{10}H_{12}Br_2N_2 + HBr$ . On treatment with potash, it yields nicotine.

**Bromonicotine**,  $C_{10}H_{12}N_2Br_2$ .—For the preparation of this compound the author recommends the following method, instead of Huber's (*Annalen*, 131, 257), which does not yield very good results. To 50 grams of bromine and 30 grams of water are added a solution of 16 grams of nicotine in 20 grams of water in small quantities at a time, the temperature not being allowed to rise above 50—60°. The whole is warmed on a water-bath until the oil so formed is dissolved, and then 60—70 grams of water are added; on cooling a crystalline body separates out, probably the compound  $C_{10}H_{12}Br_2N_2 \cdot 2HBr$ . This is decomposed by aqueous ammonia, and yields bromonicotine. The author is at present engaged in the study of the oxidation-products of this body. P. P. B.

**Compounds belonging to the Creatine and Creatinine Groups.** By E. DUVILLIER (*Compt. rend.*, 91, 171—173).— *$\alpha$ -Hydroxybutyrocyanamine*,  $NH_2.CO.NH.CO.CH(NH_2).CH_2Me$ , a homologue of glycocyamine, may be prepared by adding cyanamide to a cold saturated solution of amido- $\alpha$ -butyric acid, then a few drops of ammonia, and allowing the mixture to stand. After about a month, the crystals of the new compound are collected, washed with alcohol, and purified by crystallisation from water containing a little ammonia. It forms long slender needles, sparingly soluble in cold water, but easily in dilute acids, almost insoluble in alcohol or ether.

*$\alpha$ -Hydroxybutyrocyanidine*,  $NH : O : N.CO.CH(NH_2).CH_2Me$ , is easily prepared by boiling the corresponding cyanine with dilute sulphuric acid: the sulphuric acid is then removed by treatment with barium carbonate, the solution evaporated to dryness, and the new cyanidine dissolved out of the residue by alcohol. It crystallises from water in long transparent needles of the formula  $C_6H_9N_3O + H_2O$ , which lose their water of crystallisation at 150°.

*Isohydroxyvalerocyanamine*,  $C_6H_{11}N_3O_2$ , forms short prismatic crystals resembling the corresponding butyric compound in properties. It is prepared in a similar manner, and when boiled with sulphuric acid is converted into the *isohydroxyvalerocyanidine*,  $C_6H_{11}N_3O + \frac{1}{2}H_2O$ .

Strecker and Erlenmeyer regard the creatines and creatinines as substituted guanidines; but the author considers that they are ureides of amido-acids, and represents their constitution by the formula given above. C. E. G.

**Hypoxanthine from Albuminoid Bodies.** By G. SALOMON (*Ber.*, 13, 1160—1163).—The author, whilst replying to the criticism of Drechsel (*Ber.*, 13, 210) on a former communication (this Journal, 36, 176), adds the following as a further proof of the production of hypoxanthine from albuminoid bodies. When fibrin is treated with pepsine and hydrochloric acid and the syntonine is removed, a solu-

tion is obtained which gives no precipitate with ammoniacal silver solution; if, however, a milligram of pure hypoxanthine be added, an immediate precipitate is obtained, thus proving that hypoxanthine does not occur ready formed in the fibrin. P. P. B.

**The Form in which the Cinchona Alkaloids occur in the Bark.** By J. E. DE VRIJ (*Arch. Pharm.* [3], 16, 34—39).—On evaporation, the aqueous extract of *Cinchona succirubra* yields a white solid, of which about 40 per cent. is soluble in alcohol. This alcoholic solution has an acid reaction and is laevorotatory. Reagents show the presence of quinic and quinotannic acids, and lime. The insoluble portion likewise consists of the same three compounds, but seeing that quino-tannic acid is generally readily soluble in alcohol, it is here probably in some new combination. The solubility of quinine in water, when the bark is macerated in water, is due to the presence of this acid reacting compound. E. W. P.

**Alkaloids from the Decomposition of Albumin.** By F. SELMI (*Ber.*, 13, 206, and *Bied. Centr.*, 1880, 560).—The author describes the apparatus employed, tabulates the volatile bye-products, and gives the reactions of the new bodies formed and of their combinations with hydrochloric and hydriodic acids. The hydrochlorides have a poisonous action on frogs similar to curare. J. K. C.

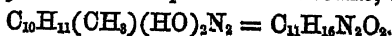
**Researches on the Alkaloids of Jaborandi Leaves.** By E. HAMACK and H. MEYER (*Annalen*, 204, 67—84).—In addition to pilocarpine, the authors have obtained a second alkaloid from the leaves of jaborandi (*Pilocarpus pennatifolius*), for which they propose the name of "jaborine." The separation of the two alkaloids depends on the facts that free jaborine is more easily soluble in ether and more sparingly soluble in water than pilocarpine, and its platinochloride more soluble in alcohol than that of the latter alkaloid; also that the compounds of jaborine do not crystallise.

The presence of minute quantities of jaborine in pilocarpine is most easily detected by its action on a frog's heart, since jaborine exactly resembles atropine in this respect.

From analyses of pilocarpine aurochloride and platinochloride the authors assign to the free base the composition indicated by the formula  $C_{11}H_{16}N_2O_2$ .

A curious fact was observed with regard to its aurochloride. When pilocarpine chloride is mixed with gold chloride, a crystalline precipitate is obtained consisting of  $C_{11}H_{16}N_2O_2 \cdot HCl + AuCl_3$ . If this is dissolved in alcohol and boiled for a time, a crystalline salt having the composition  $C_{11}H_{16}N_2O_2 + AuCl_3$ , separates on cooling.

The authors are inclined to class pilocarpine among tertiary diamines. Since the physiological action of pilocarpine is analogous to that of nicotine, experiments (which proved unsuccessful) were made to ascertain if there were any relation between its composition and that of nicotine,  $C_{10}H_{14}O_2$ . Pilocarpine might, for example, be regarded as a methyl substitution-product of nicotine, thus:—



This view is supported by the fact that jaborandi leaves yield pyridine bases among other products of their decomposition, and nicotine does the same.

Trimethylamine is formed during the dry distillation of pure pilocarpine with excess of alkali, but no coniine. Also when crude pilocarpine was distilled alone no coniine could be detected, but when distilled at 160° with excess of alkali small quantities of a body identical with coniine are formed, as stated by Poebl (*Ber.*, 12, 2185), due probably to some products of decomposition, possibly of jaborine.

*Preparation of Jaborine.*—The crude product (commercial preparation of pilocarpine, &c.) dissolved in alcohol is submitted to fractional precipitation with an alcoholic solution of platinum chloride. The first part of the precipitate which forms a hard mass, insoluble in water, is removed; the decanted liquid is again precipitated and filtered, and the solution then fully precipitated. After filtration from the precipitate, the jaborine platinochloride separates from the alcoholic solution. This salt, together with the third precipitate, is extracted with hot water and the filtrate concentrated by evaporation over sulphuric acid in a vacuum. Jaborine platinochloride is a bright yellow powder or a dark-red amorphous crumbling mass. The deeper colour is due to impurities, which can be partly removed by washing with alcohol. Another method of obtaining tolerably pure jaborine is to mix the aqueous solution of the crude substance with hydrochloric acid, filter, and add mercuric chloride until a precipitate forms. On shaking and filtering, a bright yellow liquid is obtained: sulphuretted hydrogen is added to remove the mercury, and the concentrated liquid is mixed with soda solution and shaken up with ether. On evaporation, jaborine is left as a clear colourless amorphous body. Jaborine is a very strong base, which differs from pilocarpine, especially in its sparing solubility in water and more ready solubility in ether. Its salts are soluble in water and alcohol, and do not crystallise. Free jaborine volatilises with difficulty at high temperatures. It probably belongs to the tertiary amines. The composition of jaborine is either identical with that of pilocarpine, or their empirical formulæ are closely related. It is probably contained in small quantities, together with pilocarpine in the leaves of the plant.

Compare Kingzett (this Journal, 1867, 2, 366).

G. T. A.

**Alkaloid in *Aethusa Cynapium*.** By W. BERKHARDT (*Arch. Pharm.* [3], 16, 117).—When the seeds of common fool's parsley are distilled with milk of lime, a reddish-yellow oil passes over. This oil has a strongly alkaline reaction and a very powerful penetrating odour. It appears to contain nitrogen. This alkaloid seems to have been first noticed by Ficinus (*ibid.*, 24, 257; see also *Watts' Dict.*, *Cynapine*), but he describes it as a crystalline solid, while Walz (*Neu. Jahrb. Pharm.*, 11, 351), on the other hand speaks of it as an oil.

E. W. P.

**Chemistry of the Yew.** By D. AMATO and A. CAPPARELLI (*Gazzetta*, 10, 349—355).—The green needles of the yew (*Taxus baccata*) were exhausted successively with ether, alcohol, distilled

water, and finally with dilute sulphuric acid, and each extract carefully examined. The extract left on evaporation of the ethereal solution was mixed with dilute sulphuric acid (1 : 20) and distilled in a current of steam, when an essential oil passed over resembling that of wild fennel in odour. The hot acid solution separated from the insoluble residue in the retort, deposited an amorphous powder on standing, and the filtrate from this when treated with excess of baryta and agitated with ether yielded an alkaloid. A colourless non-nitrogenous crystalline substance was extracted from the insoluble residue above-mentioned by treating it with alcohol and small quantities of animal charcoal. Its purification is a matter of considerable difficulty, and requires careful attention to details given in the original paper.

The alkaloid is a colourless, crystalline, nitrogenous substance, having a musty odour, sparingly soluble in water, but easily in alcohol or ether. Dense white fumes are produced when a rod dipped in dilute hydrochloric acid is held near it. It gives a canary-yellow precipitate with phospho-molybdic acid, and with tannin a white precipitate, which becomes crystalline on standing. Picric acid gives a yellow precipitate, and iodised potassium iodide reddish-brown crystals.

The non-nitrogenous crystalline substance forms stellate groups of needles (m. p. 86—87°), easily soluble in boiling alcohol, but only sparingly in the cold.

The solution obtained by exhausting the yew needles with alcohol after they had been extracted with ether was found to contain the same substances as the ethereal solution. From the aqueous and acid extracts, oxalic acid and small quantities of the alkaloid were obtained.

C. E. G.

**Milk Albumin and Curd Formation.** By G. MUZZO and C. MENOZZI (*Bied. Centr.*, 1880, 364—366).—The object of the author was to determine whether the albumin of milk was of the same composition as egg albumin. The albumin of milk was obtained by coagulating the casein, when the albumin remained in the whey. According to the method of Hoppe-Seyler, it is obtained by separating the casein with acetic acid and carbonic anhydride, boiling the residue, and filtering off; but the author says he obtains better results by evaporating the filtrate from the precipitated casein. After adding sodium or magnesium sulphate, by the Hoppe-Seyler method, 100 grams of milk yielded 0.5 gram, and by his own method he obtained 0.572—0.604 grams of albumin. The analysis of this albumin, as compared with that of blood, shows the following percentage composition, proving both bodies to be nearly identical.

|                  | Carbon. | Hydrogen. | Nitrogen. | Sodium. | Oxygen. |
|------------------|---------|-----------|-----------|---------|---------|
| Milk albumin.... | 53.74   | 6.95      | 15.52     | 1.55    | 22.24   |
| Blood albumin .. | 53.5    | 7.0       | 15.5      | 1.6     | 22.4    |

The authors proceed to consider the behaviour of the albumin during precipitation at different temperatures, and they find that in milk deprived of its casein by the addition of acetic or lactic acid (0.50—0.75 gram to 100 grams of milk), the slightest warming causes a pre-

cipitate in the clear whey; it takes place at so low a temperature as 3—4° C. On heating it to 40° a further precipitation takes place; again at 59·68°; at 72°; and finally at 100°. When the milk is boiled previous to being treated either with rennet or acid, the precipitate is greater than when it is not boiled and no albumin separates; but the total obtained in that case is simply the sum of the albumin and casein.

J. F.

**Peptone.** By C. A. PEKELHARING (*Pflüger's Archiv.*, 22, 185—206). The researches of Plósz, Maly, and Adamkiewicz, the author admits, point to the conclusion that albuminoids, although changed by the digestive fluids into peptones, resume after absorption their original properties, and further, that peptone may be substituted for albuminoids, as a food not only without harm, but with positive advantage to the animal. But it is obvious from the methods of preparation of peptone adopted by these observers, that the word "peptone" has not the clear and definite meaning usually attributed to it. The method used in all these cases was the digestion of fibrin by gastric juice. But the times deemed sufficient by each observer for complete conversion vary widely. Plósz, 2—3 weeks; Maly, 2—3 days; Adamkiewicz, 2—5 hours. Despite these differences, the conclusions arrived at agree in the main, viz., that peptone can replace proteids as food, and that animals so fed will not only maintain, but increase their weight.

After examining these results more in detail, the author remarks on the importance of experimenting with a substance of constant composition, and proceeds to describe his method of preparing pure peptone, which depends on a property described by Place and Huizinga (*"Onderzoekingen gedaan in het physiologisch laboratorium der Leidsche Hoogeschool,"* 1870, and *"Maandblad vooN Natuurwetenschappen,"* 1873, p. 29), viz., that in the cold a solution of peptone, having an acid reaction, is precipitated by neutral salts, the precipitate redissolving on warming.

Fibrin from bullock's blood and egg-albumin was used, and was digested with 0·2 per cent. hydrochloric acid, and pepsin (either commercial or prepared by extracting pig's or dog's gastric mucous membrane in glycerol) for 2—5 hours at 40° C. The solution was then neutralised until the reaction was very feebly acid, heated to boiling, and filtered hot. The filtrate after cooling, usually opalescent or distinctly cloudy, was evaporated a little, made strongly acid with acetic acid, and saturated with sodium chloride. The somewhat abundant flocculent precipitate so produced was filtered off, after 8—12 hours. The fluid, which filters readily, passes perfectly clear through the paper, and the precipitate dissolves very readily in distilled water on warming, still not without a slight flocculent cloudiness, due to albumin which has not been completely precipitated by boiling in a feebly acid solution, but when precipitated by sodium chloride and acetic acid, is not soluble on heating. If the precipitate is dissolved in a sufficiency of water, the fluid, when separated from the albuminoid precipitate, is perfectly clear; if, however, the distilled water be spared, with the idea of avoiding a large mass of fluid, the precipitate will return on cooling. The solution is then to be dialysed, in order to get rid of the acetic acid and sodium chloride; in one day, a precipitate of peptone



is formed, which continually increases as the dialysis is pushed, and which on warming, or the addition of small quantities of acid, alkali or salts, is completely dissolved. After three or four days' dialysis, the fluid is nearly free from salts, and the precipitate may be removed from the dialyser, boiled in water, and the resulting solution, which is not quite clear, filtered hot. The filtrate is a pure peptone solution, and will yield a heavy precipitate on cooling. It is to be concentrated at a gentle heat, and finally dried in a vacuum over sulphuric acid. When dry, peptone so prepared is a pure white powder, and is not hygroscopic. It has the following properties:—

Heated over a flame, it does not melt, but forms strong tenacious bubbles. The ash is small; the substance heated at 105° gave 0.4 per cent. and 0.47 per cent. ash.

The powder is only partially soluble in cold water, but dissolves completely on warming, separating again as the solution cools. The solution has a perfectly neutral reaction.

Addition of a small quantity of sodium chloride will prevent precipitation on cooling; added in excess, however, it causes a slight turbidity in the cold, which disappears on warming.

Very small quantities of acids or alkalis will cause solution in the cold. Peptone is precipitated from the alkaline solution by sodium chloride in excess; this does not occur, however, if the peptone is warmed in the acid solution, provided the acid is not present in too small quantity, and has acted thoroughly (this is best effected by warming); saturation with sodium chloride to the extent of 4 per cent. gives a precipitate, which completely disappears on heating. The same takes place if more salt is added. When 16 per cent. of salt has been exceeded, complete solution only occurs when the peptone solution is somewhat dilute. Peptone is precipitated from the feebly acid or alkaline solution by neutralisation; if, however, too much acid or alkali has been used for solution, sufficient salt may be formed to hinder precipitation. Strong nitric acid gives a precipitate, which vanishes on heating, before the yellow coloration appears, and returns on cooling. Silver nitrate added to a solution of peptone which is cooling, and therefore is becoming cloudy, increases the cloudiness. The precipitate disappears almost entirely on cooling; a slight opalescence, due to sodium chloride, alone remaining. The precipitate produced by silver nitrate is soluble in acetic acid.

Absolute alcohol precipitates peptone in neutral, but not in acid or alkaline solution. Potassium ferrocyanide and acetic acid give a voluminous precipitate, soluble on heating.

Basic lead acetate, with ammonia, tannic, and phosphomolybdic acids, give precipitates which are not soluble on heating.

The precipitate yielded by Millon's reagent dissolves with a red colour, if only small quantities of the mercury solution are used. More of the reagent gives a red precipitate, permanent on heating; cupric sulphate, ferric acetate, ferric sulphate, lead acetate, and basic lead acetate do not precipitate the peptone solution, unless sodium chloride or potassium acetate is present.

The author then proceeds to say that from these reactions no albumin can be present. Peptones from fibrin or albumin or other

sources resemble one another in all their chemical properties. All are lævorotatory, but there is some difference in the degree of rotation, albumin peptone having the least, and casein peptone the greatest, effect on polarised light.

No elementary analysis was made by the author. The question whether peptone is isomeric with albumin, or differs from it by one or more molecules of water, is then raised, and the experiments of Huizinga and others on the subject criticised at great length. With the view of showing that these observers did not use a pure material, Meissner's peptones are examined with the same conclusion.

W. N.

## Physiological Chemistry.

**Respiration under Reduced Pressure.** By J. SETSCHENOW (*Pflüger's Archiv.*, 22, 251—261).—The entry of oxygen and nitrogen into the blood under normal circumstances has been fairly well investigated, and Paul Bert has made some researches on the effects of compressed air; less is known of the effect of rarefaction, the chief authorities on the subject being L. Meyer, Fernet, and J. Worm-Müller. The author points out differences between figures given by the latter and some results obtained by Paul Bert, as to the relations of the oxygen in the blood to the pressure; he then refers to the death of the aéronauts Sivel and Crocé-Spinelli, at a height at which the barometer registered only one-third of an atmosphere, and describes a series of experiments with oxygen and nitrogen. The results with the former confirm those of Meyer, Fernet, and Worm-Müller. Nitrogen was found to behave to blood as to water under varying pressures, and he concludes that a pressure much below half an atmosphere cannot be borne without danger to life.

W. N.

**Hydrolytic Ferments of the Pancreas and Small Intestines.** By H. T. BROWN and J. HERON (*Chem. News*, 42, 63—67).—The authors confirm the results of Musculus and De Mering (*Bull. Soc. Chim.*, 31, 105) on the hydrolytic action of the pancreatic secretion. They find that starch is converted into maltose and dextrose, the latter being a product of the action of the secretion on the maltose. Its action, however, differs from that of malt extract on starch, since in the latter case maltose is the final product.

The pancreatic secretion has no action on cane-sugar, if organic life be excluded; but if the digestion be continued sufficiently long to develop bacteria, evolution of gas takes place.

Extracts of the small intestines of a fasting animal have little or no hydrolytic action on starch or cane-sugar; but in the case of an animal killed during the process of digestion, the extract has a somewhat greater action. The intestine itself possesses far more pronounced hydrolytic action than its extract; different portions of the intestine act differently on cane-sugar.

The portion of duodenum below the pylorus, containing Brunner's glands, acts after digestion for 16 hours in the cold, and 5 hours at 45°. The duodenum below Brunner's glands, acts after digestion for 16 hours in the cold. The jejunum without Peyer's patches, and the ileum, acts after 3½ hours' digestion at 40°. Peyer's patches act after 1½ hours' digestion, at 40°.

Portion of the small intestines act on starch in a manner similar to the pancreatic secretion; maltose is first formed, and the final product is dextrose into which the former is rapidly converted. The small intestine acts more rapidly and completely on maltose than on cane-sugar, in which case the action ceases when 25 per cent. of the total quantity of cane-sugar has been inverted, whilst in the former case the action is continuous.

The actions of the pancreas and small intestine on starch are mutually dependent on each other, for whereas the pancreatic secretion rapidly converts starch into maltose, it only very slowly and partially converts maltose into dextrose; this conversion is, however, readily effected by the small intestine.

The variability of the hydrolytic action of the different portions of the intestines is dependent on the frequency of either the Lieberkühn or Brunner glands, but appears to be correlative with the distribution of Peyer's glands.

L. T. O'S.

**Nutritive Value of Fluid Meat.** By M. RUBNER (*Zeits. f. Biologie*, 15, 484—492).—The general properties of the so-called fluid meat having been described, the author gives tables of analysis, comparing it with meat and meat extract; 12·61 per cent. of NaCl was found:—

|                              | Fluid<br>meat. | Fluid meat<br>after<br>removal of<br>NaCl. | Meat. | Meat<br>extract. |
|------------------------------|----------------|--|-------|------------------|
| Water .....                  | 20·79          | —  | 75·90 | 21·70            |
| Dry substance .....          | 79·21          | —  | 24·10 | 78·80            |
| N in 100 pts. dry substance. | 10·36          | 11·86                                      | 14·10 | 10·25            |
| Alcohol extract .....        | 43·30          | 49·54                                      | 6·66  | 70·39            |
| Ash .....                    | 18·64          | 6·90                                       | 5·39  | 22·86            |
| Organic matter .....         | 81·36          | 93·10                                      | 94·61 | 77·64            |
| N in 100 pts. organic matter | 12·73          | 12·73                                      | 14·91 | 13·21            |

The inorganic constituents of 100 parts of the dry substance, after removal of the NaCl as compared with meat, was found to be as follows:—

|                                     | Fluid meat.<br>NaCl removed. | Meat. |
|-------------------------------------|------------------------------|-------|
| SiO <sub>2</sub> .....              | 0·051                        | 0·432 |
| F <sub>2</sub> O <sub>3</sub> ..... | 0·021                        | 0·053 |
| CaO .....                           | 0·026                        | 0·093 |
| MgO .....                           | 0·162                        | 0·178 |
| PO <sub>5</sub> .....               | 0·715                        | 1·852 |
| SO <sub>3</sub> preformed .....     | 0·112                        | —     |
| SO <sub>3</sub> in the ash .....    | 1·758                        | 2·250 |

The quantity of peptone present is important. This was estimated by Schmidt's method (Du Bois, *Archiv.*, 1879, 8, 39), and the general results are contained in the following table:—

100 parts fluid meat contain—

|                      |                     |
|----------------------|---------------------|
| Water .....          | 20·8                |
| Dry residue .....    | 79·2                |
| Ash .....            | 14·8 with 10·0 NaCl |
| Organic matter ..... | 64·4                |
| Peptone.....         | 23·8                |
| Extractives .....    | 40·6                |

As a result of his investigations, the author concludes that fluid meat is very like meat extract plus peptone, and after mentioning the peptone preparations of Sanders-Ezn, Adamkiewicz, and Leube and Rosenthal, he points out that the cost of sufficient fluid meat, as a substitute for the ordinary proteid of an average man for one day, would not be less than 10s., and expresses the opinion that the peptone is the really important element; it can never come into general use as a food stuff at the price, and will not supersede Liebig's extract for other purposes.

W. N.

**The Proteid required by the Average Workman.** By H. C. BOWIE (*Zeits. Biologie*, 15, 459—484).—The author criticises at great length the objections raised by G. R. Beneke to the standard diet for a man doing moderate work, suggested by Voit (118 grams albuminoids, 56 grams fat, 500 grams carbohydrates per diem). This being in his (Beneke's) opinion too much.

W. N.

**Influence of Lactic Acid in Fodder.** By SIEDAMGROTZKY and V. HOFMEISTER (*Bied. Centr.*, 1880, 373—374).—Experiments were undertaken to discover the effects of lactic acid on the bones of animals, and they are of a certain importance in view of the frequent employment of factory residues rich in starch as fodder, such substances being easy of decomposition in the intestinal canal and forming lactic and other acids there; the subjects of experiment were goats and sheep, and it was shown that the presence of the acid exerts a solvent effect on the bones, more especially on those of young and growing animals; with sucking animals the effects cannot be estimated, as they could not be prevailed on to eat the food; the lime and phosphates were principally attacked, the magnesia untouched, but rhachitis and osteomalacie were not induced by the use of this food.

J. F.

**Formation of Sugar in the Liver.** By J. SEEGEN and F. KRATSCHEMER (*Pflüger's Archiv.*, 22, 214—239).—The authors have

already endeavoured to show that the liver-sugar is grape-sugar, whilst the sugar which is formed by the action of all diastatic ferments, diastase, ptyalin, pancreatic ferment, &c., on starch or glycogen differs from grape-sugar in its reducing power and specific rotation; probably the sugars so produced are all identical with maltose (Dubrunfant, O'Sullivan, Schultze). There are, however, slight differences according to the method of preparation, and the question is: Is the sugar obtained from the dead liver a ferment sugar, or true grape-sugar?

The sugar found in the liver closely resembles that produced by the action of acids on glycogen: hence the existence of acid in the liver is of importance. A series of experiments are given, which show that side by side with the increase of sugar in the liver after death there is an increase in the acidity.

The action of the acids extracted from the liver on glycogen were next investigated. The liver was prepared by the Liebig-Scherer method. A strong glycogen solution heated with lactic acid was not affected, but when the two were placed together in a sealed tube and heated at 100° C. for 24 hours, sugar was produced. The method of treating the liver, preparing the extract, and surmounting the difficulties of the sugar and glycogen estimation, are then described at length. The possibility that the sugar and glycogen formation was not the same in all parts of the liver was next investigated; Wittich's experiments are referred to (*Centralblatt med. Wiss.*, 1875, No. 8). Analyses of a whole liver, divided into 4 parts, are given; and the authors conclude that the formation is regular and equal in all parts of the organ.

Dogs were used for the experiments, being poisoned by potassium cyanide, and the livers excised whilst the heart was still beating; they were then cut into small pieces, and treated by the method described, at intervals varying from two minutes to six days after excision. Five dogs were used, and were fed ( $\alpha$ ) on bread, ( $\beta$ ) on flesh, and ( $\gamma$ ) starved.

The percentage of sugar found in the liver two or three minutes after excision was 0.46 to 0.55 in *all* cases, *i.e.*, the nature of the diet does not appear to affect the quantity found so shortly after death.

The percentage of sugar rises slowly for some time after death, most rapidly during the first hour or two. In the starved animal there was no further increase after the first 24 hours.

The estimation of the total sugar plus the sugar obtained by the acids on the glycogen in sealed tubes, gave remarkable results. If the sugar arises entirely from the conversion of glycogen, the quantity found by this method should be the same for all the pieces; but this is *not* the case, and therefore the authors argue from this, and the fact that in their experiments the rise in the sugar did not correspond to the fall in the glycogen, but was greater than could be accounted for in this way, that there must be some source of sugar in the liver other than glycogen. The experiments show further a steady rise in the acidity of the liver after death.

Experiments on rabbits yielded somewhat different results. The quantity of glycogen found was so much greater than in the dogs that the experiment was repeated four times, under the impression that some mistake had been made, but always with the same result, the

quantity of glycogen amounting to more than twice as much as was found in the dogs' liver. Experiments on cats yielded much the same results as those on dogs.

The authors sum up their results as follows:—

(1.) In *all* the animals experimented on, the liver, when taken out with all possible speed, was always found to contain from 0·5 to 0·6 per cent. of sugar.

(2.) That the liver-sugar is not entirely derived from glycogen, but has some other source.

(3.) That not only the liver-sugar, but any carbohydrate which by heating with acids can be converted into sugar (glycogen or dextrin) can be formed afresh in the dead liver.

(4.) The liver glycogen experiences a considerable diminution about 48 hours after death.

(5.) An energetic transformation of glycogen, immediately after death, occurs only in rabbits.

W. N.

**Some Ingredients of Normal Urine.** By C. SCHIAPPARELLI and G. PERONI (*Gazzetta*, 10, 390—392).—As it is well known that lithium, cæsium, and rubidium are almost always associated with the alkaline metals, and that in some minerals, and in bones and plants, cerium, lanthanum, and didymium are associated with calcium, the authors have examined human urine to see if the same association of metals occurred in it; 600 kilos. of urine were evaporated, and the incinerated residue carefully analysed. Rubidium and cæsium were found, and lithium in smaller quantity; also cerium, lanthanum, and didymium, with a trace of manganese. The authors consider that in normal urine copper only occurs in infinitesimal quantity.

C. E. G.

**Influence of Borax on the Decomposition of Albumin in the Organism.** By M. GRUBER (*Bied. Centr.*, 1880, 509—510).—Experiments on animals showed that the quantity of urine secreted increased with the amount of borax given with the food, and the decomposition of albumin was consequently increased. Borax does not seem to affect the digestion or injure the appetite.

J. K. C.

**Influence of Fodder on the Secretion of Milk.** By W. FLEISCHMANN (*Bied. Centr.*, 1880, 510—515).—A herd of cows nearly at the end of the milking period, having been for some time previous supplied with an insufficient quantity of fodder, were allowed a larger amount, the result being that the quantity of milk yielded by them was also increased, but not to such an extent as to repay the extra cost. In the case, however, of another herd, all of which were at the beginning of the lactation period, an increase of the quantity of fodder (previously insufficient) was attended with a corresponding increase in the quantity of milk more than sufficient to repay for the added cost of food; the quality of the milk was also greatly improved.

J. K. C.

**Influence of Arsenic on Animals.** By C. GIES (*Bied. Centr.*, 1880, 372—373).—The author experimented with rabbits, cocks, and swine, constantly increasing quantities of arsenic acid being mixed with their food for nearly four months; all the animals became fatter,

the growth of bone in the younger animals was constant, and in cases where under normal conditions there would have been a spongy growth, these animals had compact bone substance. Stall fed animals showed the phenomenon very markedly, the arsenic was freely eliminated through the skin and lungs; full-grown animals showed a pronounced thickening of the corticalis diaphysis, and a fatty condition of the muscles of the heart, the liver, kidneys, and spleen; when the doses were further increased, symptoms of chronic poisoning appeared.

J. F.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of Oxygen on Fermentation.** By A. MAYER (*Ber.*, 13, 1163—1164).—When the fermenting liquids contain only sugar and yeast cells, the author finds that oxygen aids fermentation, inasmuch as it favours the growth of the yeast plant. When yeast cells lose their power on account of the concentration of the sugar solutions, it is restored by adding some sodio-potassic tartrate. This observation, the author considers, throws some light on the fact that artificial fermentation mixtures work more slowly than in the preparation of wine, &c. Also that the experiments on the influence of oxygen need to be repeated with the addition of organic acids.

P. P. B.

**Lower Organisms in the Air.** By E. C. HANSEN (*Bied. Centr.*, 1880, 546—547).—Flasks partly filled with boiled beer-wort were placed under different fruit trees in summer, and were found to attract very different organisms, even when placed near to one another: some kinds of spores were found to frequent one place and some another.

J. K. C.

**Action of Light and Darkness on Tannin Solutions.** By A. R. LEEDS (*Chem. News*, 42, 41).—A standard solution of ammonium chloride under the influence of fungoid growth does not undergo any change on exposure either to light or to darkness when oxygen is excluded, whether chloroform is present or not.

Tannin solutions containing saproligneous growths, to which oxygen is freely admitted, undergo a slight change when exposed to diffused light, and in darkness change takes place to a great extent, with a large development of fungi. Chloroform slightly retards the development of the fungus. The circumstances therefore most favourable to preservation of standard solutions are exposure to light, with exclusion of oxygen and germs of fungoid growth.

L. T. O'S.

**Gelatinous Matter in Beets.** By P. v. TIEGHEM (*Bied. Centr.*, 1880, 337—339).—This paper is a review of Scheibler's discovery of this remarkable substance, which he has named from its properties "frogspawn." He considered it to be the protoplasm of the beet, out of which a new carbohydrate, "dextran," has been separated. Borscow, on the other hand, takes a different view, and asserts that this gelatinous matter has neither the physical properties nor chemical com-

position of protoplasm, particularly because of its non-nitrogenous character. He considers it to be a substance of a pectose nature, having its origin in the cells of the beet. Another observer shares the error, and Durin also asserts that the substance is non-nitrogenous. He calls it "cell matter," and thinks it is produced by spontaneous fermentation of the cane-sugar in the root.

Previous to those observers, however, two French chemists, Jubert and Mendis, had arrived at sounder conclusions on the subject, and expressed their conviction that this beet-jelly was a plant of a distinct character. The author confirms this view, and names the plant *Leuconostoc mesenteroïdes*, and describes it as being produced in the juice during the manufacture of sugar, with the aid of the dissolved oxygen; he finds that it inverts the sugar and nourishes itself upon it, being a powerful medium of inversion. It is on that account a dreaded enemy of the sugar industry, and every possible means should be taken for its destruction.

J. F.

**Fermentation Theory of Nitrification.** By J. H. STORER (*Biol. Centr.*, 1880, 388—389).—The author offers these experiments as a confirmation of Schlösing's theory of nitrification. Eleven flasks, well corked, with inlet and outlet tubes, were connected in series, some of them containing peat, viz., No. 8, peat with ammonium chloride, No. 9, peat with oxide of iron, No. 10, peat with both ammonium chloride and oxide of iron, the others different combinations of ammonia, clear water, &c. Oxidising agents were drawn through the series by an aspirator for eleven days. Those flasks which contained peat were the only ones which yielded nitrogen reactions. The same experiments were repeated with peat which had previously been treated with warm acids, the results in this case being negative, further confirming Schlösing's theory that the ferments in the peat were destroyed by the acid.

J. F.

**Influence of Atmospheric Electricity on the Growth of Plants.** By C. NAUDIN (*Biol. Centr.*, 1880, 336—337).—Grandean by his experiments showed that the blooming and fruiting of plants was retarded or accelerated by the fact of atmospheric electricity being allowed access or not to certain plants.

The author of this paper does not exactly contradict Grandean's conclusions as far as the plants which he (Grandean) experimented on, but the results of the later experiments are calculated to throw doubts on the general application of any rules as yet discovered. Naudin's observations were made at Antibes, in the south of France, whilst Grandean's were made at Nancy, in the north-east. The field was quite open, no high object in the neighbourhood. The apparatus for keeping off electricity was an iron cage, which let in less light than Grandean's arrangement. The plants were French beans, lettuce, and tomatoes, some of which were planted under the cage and some outside, but the other conditions were exactly similar. As already indicated, the results of the crop were that the plants which were sheltered from atmospheric electricity were in every respect superior to those grown in the open.



The author thinks that the injurious effect of trees on vegetation is not due to their effect in keeping away electricity, but finds a ready solution in their shadow, and the exhaustion and drying up of the soil by their extended roots. On the other hand, many plants seek and thrive best in the shade of trees. The question of the effect of atmospheric electricity is still in a very unsettled state, and probably varies with the species of plant, the climate, &c., and while our experience is so limited the promulgation of generalities on the subject should be avoided. J. F.

**Energy of Assimilation in Plants.** By C. A. WEBER (*Bied. Centr.*, 1880, 378).—The green leaves of the higher orders of plants by their activity in assimilation produce their combustible constituents. These, minus the ash, are generally taken as the measurement of the energy; but the experiments made by the author lead him to believe that there is a considerable difference between the powers of assimilation in different species of plants. Those actually experimented on were *Tropæolum majus*, *Phaseolus multiflorus*, *Ricinus communis*, and *Helianthus annuus*. J. F.

**Formation of Chlorophyll in the Dark.** By C. FLAHAULT (*Bied. Centr.*, 1880, 556—557).—The author suggests that the chlorophyll in the young shoots of certain plants which have grown in the dark was already formed in the seed while still connected with the plant. J. K. C.

**Chlorophyll in Epidermis of Foliage of Phanerogams.** By A. STÖHR (*Bied. Centr.*, 1880, 376).—Chlorophyll was found in the epidermis of the leaves of 94 out of 102 specimens of dicotyledons and broad-leaved Gymnosperms, but was not detected in the narrow-leaved species, or in monocotyledons. It was found chiefly in the cells of the under leaves, the leaf-stalks and the stems; that which existed in the cells of the upper surface of the leaves had been decomposed by the action of intense light. It was formed by the aggregation of green protoplasmic matter to the starch corpuscles; the starch was modified afterwards, but the chlorophyll showed no assimilation energy. J. F.

**Influence of Annual Temperature on Change of Colour in Leaves.** By H. HOFMANN (*Bied. Centr.*, 1880, 378—379).—If a thermometer be freely exposed to sunlight, and the readings above 0° C. added together from the 1st of January to the day in autumn when the turn of the leaf is general, and the same practice pursued for several years, a curve can be constructed which will show considerable variations. If then another curve is constructed below it, composed of the various days on which the change of colour became general, there will be found a correspondence which cannot be accidental, but which, on the contrary, has been confirmed by so many observations, that the author does not hesitate to formulate it as the expression of a law. The temperatures of January and February, the time of rest for plants, cannot exercise any influence, neither is it probable that of April or May does so, when the leaves first appear,

and as there is no regular interval of time between the budding of the leaves and their turn, the few weeks immediately previous to that period are the most important. The more cloudy the autumn, and the lower the sum of the temperature of the last month of it, the longer the leaves remain green. The author draws attention to similar results to be observed with plants grown in shade, although their behaviour under such conditions is not so regular. J. F.

**Breathing of Plants and Animals.** By J. JAMIESON (*Bied. Centr.*, 1880, 374).—The author, in a memorial submitted to the Royal Society of Victoria, traces certain resemblances between the breathing of plants and of animals, and says that in the same manner as the inhaled oxygen combines with the hæmoglobulin of the blood of animals and forms more active combinations of the character of ozone, so does it combine with some fluid in plants, which fluid has not yet been identified, but that the presence of ozone in the ripe fruit can be detected by any of the ordinary tests, such as guaiacum or iodide of starch. J. F.

**Intramolecular Respiration of Plants.** By J. WORTMANN (*Bied. Centr.*, 1880, 554—555).—From experiments made with young shoots of *Vicia faba* and *Phaseolus multiflorus*, the author concludes that the carbonic anhydride given off by plants is referable to intramolecular action alone, and is independent of atmospheric oxygen, that the albumin converts the carbohydrates into alcohol with evolution of carbonic anhydride; the alcohol by means of atmospheric oxygen is converted into acetic acid, and by consolidation and rearrangement of the molecules of the latter, carbohydrates are again formed. J. K. C.

**Influence of Continuous Sunlight on Plants.** By SCHÜBELER (*Bied. Centr.*, 1880, 521—523).—The results of the transporting of southern plants to arctic regions, where they enjoy a lengthened period of unbroken sunlight, are that the development of the pigments and aroma of the plants and fruit is greatly increased, whilst the sweetness of the latter is much diminished. The ripening process is also quickened. J. K. C.

**Functions of Vegetable Ducts.** By J. BÖHM (*Bied. Centr.*, 1880, 526—529).—The author, after stating that the original function of the ducts in growing plants is for the conveyance of sap, and not of air, and that as the tubes become older, air finds an entrance, proceeds at some length to give the conditions under which the passage of water through the ducts occurs. J. K. C.

**Influence of Salts on the Absorption of Water by Roots.** By J. VESQUE (*Bied. Centr.*, 1880, 556).—Under normal conditions plants absorb moisture more quickly from distilled water than from saline solutions; but after being for some time in the former, they absorb water more rapidly from salt solutions, and *vice versâ*. J. K. C.

**Quantity and Distribution of Water in Trees.** By N. GELEZ-  
NOW (*Bied. Centr.*, 1880, 379).—The author's experiments were made  
on trees 11 to 35 years old of the species *Acer platanoides*, *Betula alba*,  
and *Populus tremula*; he found that the amount of moisture increases  
from the bottoms to the tops both of stems and branches, the extreme  
points, however, being drier than the part immediately below, and the  
extreme base somewhat damper than the portion immediately above  
it. In the bark, this law is observed even more strictly than in the  
wood, the author having found no variations from the before-men-  
tioned rule. The relative moisture of bark and wood varies very  
much in different trees; the wood of the fir is damper than the bark;  
with the maple, the reverse is the case. The wood of the fir contains  
more moisture than that of any of the other trees examined, containing  
in winter 64.5 per cent., in spring and autumn 63 per cent., in summer  
60 per cent.; maple in spring 44.4 per cent., in winter 37.1 per cent.  
The birch similarly shows less moisture in winter than in summer,  
advancing from 46.4 per cent. to 71.8 per cent. in the month of May.

J. F.

**Sap of Trees and Specific Gravity of their Wood.** By  
NÖRDLINGER (*Bied. Centr.*, 1880, 379—381).—The presumption that  
the dryness or heavy rainfall of the preceding winter has an effect  
on the quantity of sap in trees has been found to be erroneous. The  
author has constructed a graphic curve which shows a regular propor-  
tion, irrespective of rainfall or weather, all the trees observed show-  
ing a decided falling off in quantity at the end of the year, changing  
to an increase as the winter passed away, and continuing into the  
summer.

The *minimum* quantities of sap contained in different trees does not  
appear to vary in proportion to their specific gravities, the beech with  
one-third greater sp. gr. (dry) than the hazel shows the same minimum  
contents of sap, and the denser mulberry contains more than the hazel.  
The *maximum* sap-content, however, is different, being higher in the  
soft and porous than in the hard and denser kinds; trees with needle  
foliage showed the least variation in both their maxima and minima.

The differences of dry and green weight of the various woods ex-  
amined is less during the course of the year than the variations of  
sap-contents. The author has constructed graphic curves showing  
these variations.

J. F.

**Relation between the Starch, Phosphoric Acid, and Mineral  
Constituents of the Potato.** By H. PELLET (*Compt. rend.*, 90,  
1361—1363).—The results of the analyses of H. Joulie, which were  
undertaken with an entirely different object, having been placed at  
the disposal of the author, have been recalculated by him so as to  
exhibit, firstly, the relation existing between the starch and mineral  
constituents of the potato tuber, and secondly, the unvarying composi-  
tion of the whole vegetable when the constituents are referred to 100  
kilos. of starch.

| Potatoes named "Van-der-Veer," grown at<br>Chevrières (Oise), 1879. |         |        |  |       |      | Red mealy potato grown at Verrières (Seine<br>and Oise), 1877. |        |        |  |       |   |
|---|---------|--------|--|-------|------|--|--------|--------|--|-------|---|
| Tubers.   |         |        | Tops.  |       |      | Tubers.  |        |        | Tops.  |       |   |
| kilos.  |         |        | kilos.   |       |      | kilos.   |        |        | kilos.   |       |   |
| Total.  |         |        | Total.   |       |      | Total.   |        |        | Total.   |       |   |
| Per 100<br>kilos. of<br>starch.                                     |         |        | Per 100<br>kilos. of<br>starch.                |       |      | Per 100<br>kilos. of<br>starch.                                |        |        | Per 100<br>kilos. of<br>starch.                |       |   |
| $H_2SO_4$<br>required<br>to saturate<br>bases.                      |         |        | $H_2SO_4$<br>required<br>to saturate<br>bases. |       |      | $H_2SO_4$<br>required<br>to saturate<br>bases.                 |        |        | $H_2SO_4$<br>required<br>to saturate<br>bases. |       |   |
| Weight of fresh crop.....   | 14,000  | 8,200  | 17,200   | —     | —    | 27,510   | 29,850 | 57,860 | —  | —     | — |
| " dried ".....  | 2,925.6 | 1,880  | 4,765.6  | —     | —    | 6,058  | 2,049  | 8,107  | —  | —     | — |
| Number of plants to the hectare.....                                | 20,000  | —      | —  | —     | —    | 30,000   | —      | —      | —  | —     | — |
| Phosphoric acid.....  | 13.78   | 8.06   | 21.84  | 1.04  | —    | 89.37  | 7.868  | 47.215 | 1.072  | —     | — |
| Lime.....   | 6.46    | 69.12  | 74.58  | 8.57  | 5.06 | 8.877  | 53.786 | 57.663 | 1.308  | 1.867 | — |
| Magnesia.....   | 1.08    | 15.06  | 16.14  | 0.76  | 1.52 | 6.721  | 12.642 | 19.366 | 0.439  | 0.878 | — |
| Soda.....   | 0.00    | 1.14   | 1.14   | 0.05  | 0.06 | 9.389  | 10.204 | 19.593 | 0.144  | 0.577 | — |
| Potash.....   | 45.20   | 7.06   | 52.26  | 2.50  | 2.12 | 190.9  | 74.15  | 265.10 | 6.015  | 6.111 | — |
| Ferric oxide.....   | 8.74    | 7.08   | 10.82  | 0.51  | 8.76 | 1.576  | 7.560  | 9.136  | 0.207  | 8.423 | — |
| Silica.....   | 44.50   | 182.0  | 226.5  | 10.86 | —    | 76.683   | 16.164 | 92.797 | 2.105  | —     | — |
| Total ash + $SiO_2$ .....   | 121.04  | 342.0  | 463.04   | 22.35 | —    | 345.06   | 382.0  | 727.66 | 16.497   | —     | — |
| Total ash - $SiO_2$ .....   | 76.86   | 116.78 | 193.64   | 9.28  | —    | 263.98   | 171.97 | 435.85 | 9.88   | —     | — |
| Nitrogen.....   | 47.38   | 22.64  | 70.02  | 3.85  | —    | 72.938   | 22.908 | 95.846 | 2.174  | —     | — |
| Sulphuric acid.....   | 7.60    | 9.26   | 16.86  | 0.80  | —    | 11.991   | 5.767  | 17.751 | 0.403  | —     | — |
| Percentage of dry substance in the tuber....                        |         |        |  |       |      | 22.02  |        |        |  |       |   |
| Deduct.....   |         |        |  |       |      | 6.00   |        |        |  |       |   |
| Difference (starch).....  |         |        |  |       |      | 16.02  |        |        |  |       |   |
| Total starch per hectare.....                                       |         |        |  |       |      | 4407.0 kilos.  |        |        |  |       |   |

From these tables it will be seen—

1. That there is a constant relation between the total phosphoric acid derived from the whole plant and the starch.

2. That there is also a relation between the starch and the total mineral constituents, the silica being deducted.

3. That there are great differences in the proportions of the principal alkalis, potash and lime, when calculated to 100 kilos. of starch, but that there is an *equivalent substitution* for these alkalis, so that the quantity of sulphuric acid necessary to saturate all the bases is sensibly the same.

4. That these relations exist in different sorts of potatoes grown on different soils and in different years.

5. That the silica and nitrogen vary between considerable limits, as has already been shown in the case of beetroot.

Another variety of potato, called "chardon," gave likewise 1.1 kilos. of phosphoric acid per 100 kilos. of starch, whilst the "rose hâtive" yielded 0.989 kilo. of phosphoric acid; the ash of the former, without the silica, was 8.22 kilos., and that of the latter 7 kilos.

The interesting point in connection with these analyses is that the relation, 1.1 kilos. of phosphoric acid to 100 kilos. of starch, is sensibly identical with the relation between the phosphoric acid and sugar in the sugar-beet.

J. W.

**Calcium Oxalate in Plants.** By B. J. VAN DER PLOEG (*Bied. Centr.*, 1880, 556).—In the leaves of many plants the lime increases in the ash with the age of the leaf from 6 to 9 per cent., but is unaccompanied by a proportionate increase of oxalic acid, and appears to have no connection with the amount of the latter substance present.

J. K. C.

**Presence of Alcohols and Hydrocarbonss in Plants.** By GUTZERT (*Bied. Centr.*, 1880, 377).—The author discovered ethyl and methyl alcohols in the distillates from the fruits of the *Heracleum giganteum*, *Pastinaca sativa*, and *Anthriscus Cerefolium*, and also ethyl butyrate in the lowest boiling fraction of the heracleum oil. He dismisses as unfounded the supposition that these have been formed during the process, but believes they exist in a free state in the plants. The author also proves the existence of a hydrocarbon of the general formula  $C_nH_{2n}$ , and has discovered a new body which he calls *heraclin*. This substance does not contain nitrogen, is devoid of smell and taste, and is of the empirical formula  $C_{22}H_{22}O_{10}$ ; melts at  $185^\circ$ , and crystallises out of an alcoholic solution in star-shaped groups of silky needles, which are at first white, but become yellow on exposure to light.

Heraclin is indifferent to litmus, insoluble in water, but easily soluble in chloroform, with difficulty in cold ether, carbon bisulphide, and alcohol. Concentrated sulphuric acid yields a deep gold-coloured solution, from which it separates on the addition of water. Heraclin, as also the hydrocarbon above mentioned, is found in the fruits of *H. giganteum*, *H. spondylium*, and *Pastinaca sativa*. Further experiments are promised, to show whether it varies in quantity with the ripeness of the fruit and also with the quantities of alcohol present.

J. F.

**Composition of the Ashes of the Trunk, Leaves, and Fruit of the Orange and the Mandarin Orange.** By L. RICCIARDI (*Gazzetta*, 10, 265—279).

**Analyses of the Ash of Certain Spice Seeds.** By C. EDZARDI (*Bied. Centr.*, 1880, 382—383).

|   | Coriander,<br>per cent. | Fennel,<br>per cent. | Dill,<br>per cent. | Carraway,<br>per cent. |
|---|-------------------------|----------------------|--------------------|------------------------|
| Amount of ash in air-dried<br>substance ..... | 4·76                    | 7·69                 | 6·31               | 5·33                   |
| Potash .....                                  | 35·16                   | 31·96                | 31·61              | 26·31                  |
| Soda .....                                    | 1·28                    | 2·38                 | 2·11               | 6·54                   |
| Lime .....                                    | 22·10                   | 19·54                | 26·51              | 18·04                  |
| Magnesia .....                                | 12·21                   | 14·08                | 7·45               | 8·27                   |
| Oxide of iron .....                           | 1·18                    | 2·12                 | 1·96               | 3·57                   |
| Phosphoric anhydride .....                    | 18·55                   | 16·47                | 17·32              | 24·29                  |
| Sulphuric " .....                             | 6·54                    | 9·98                 | 6·72               | 5·39                   |
| Silicic " .....                               | 1·03                    | 0·87                 | 2·50               | 4·98                   |
| Chlorine ... ..                               | 2·51                    | 3·41                 | 4·88               | 3·10                   |

The composition and quantities of ash resemble those of the seeds of the esparset, fodder beet, sugar beet, &c. J. F.

**Sweet Potato.** By H. ENDEMANN and G. A. PROCHAZKA (*Chem. News*, 42, 8).—The sweet potato rot is produced by the parasite *Mucor mucedo*. The mycelium of the parasite travels to a certain distance into the interior of the plant where it disappears, and the potato is rapidly destroyed by Bacteria. *Aspergillus niger* produces a similar result, but is not so rapid in its action. *Aspergillus glaucus* and *Penicillium glaucum* do not produce sweet potato rot. From the authors' researches, it appears that cane-sugar is produced, although Ledour states that the sugar formed is glucose. L. T. O'S.

**Influence of the Manure on Potato Disease, and the Starch in the Potato.** By M. MÄCKER (*Bied. Centr.*, 1880, 501—504).—Experiments carried on with the view of ascertaining the influence of different kinds of manure on potato disease, showed that in the cases under investigation Chili saltpetre especially favoured the spread of the disease. This, however, might perhaps be better accounted for by the different depths and different soils in which the potatoes were placed, as experiments of a few years back showed that with the same manure the percentage of diseased potatoes varied from 4 to 17. As regards the quantity of starch in potatoes, this was found to be very little affected by any of the manures employed, and varied more with the sort of potato under investigation. J. K. C.

**Influence of Ethyl Iodide on Germination.** By C. RABUTEAU (*Bied. Centr.*, 1880, 375).—The influence of this compound is to pre-

vent germination. A quantity of the seeds of the watercress sown on a sponge in damp sand in a vessel supplied with clean pure water germinated in two days, but ceased growing when ethyl iodide in water was put into the bottom of the vessel. The behaviour of the substance with plants is similar to ether, chloroform, and ethyl bromide; it acts on the animal organism in the same manner as chloroform.

J. F.

**Analyses of Norwegian Hay.** By W. DIRKS (*Bied. Centr.*, 1880, 331—332).—A report of the examination of certain samples of forest hay from different districts in Norway. One of the samples was from a person who had fed cattle upon it with the simple addition of straw, and found his herd subject to weakness of the bones. The composition of the different samples showed, in comparison with ordinary meadow hay, an abnormal proportion of silica, with only about one-third of the average quantity of lime and phosphoric acid generally found in good fodder. Should cows be fed solely upon this hay, there would be barely enough phosphoric acid for their daily needs. If they should be heavy milkers or with calf, the quantity would be insufficient, and the result would be a weakening of the bones and liability to fracture. The addition of bone meal or fish guano to the hay is recommended, or the employment of some other highly concentrated fodder.

J. F.

**Digestibility of Oat-straw, Hay, and Pea Holms.** By E. WOLFF and others (*Bied. Centr.*, 1880, 328—330).—The consumption of different kinds of straw by sheep has been little investigated, and the question presents difficulties, owing to the different quantities given to the animals. The oat-straw used in the experiment was fully ripe, rather strong and coarse; the pea holms contained some leaves and half-formed pods, and was consequently proportionately more tasty and nourishing; the meadow hay was of an ordinary and average character. The animals were two wethers of the bastard Wurtemberg breed, 10 months old. The consumption and the digestibility of the pea holms was far better than that of the oat-straw, and as a food fully equal in every respect to good average meadow hay, young growing sheep could supply the requirements of their growth on the former, but the meadow hay alone was not sufficient nourishment as a constant food. It is, however, probable that older animals might have consumed positively and relatively larger quantities with advantage; the oat-straw also was of a coarse nature.

J. F.

**Disease in Sheep caused by Lupines.** By F. KROCKER (*Bied. Centr.*, 1880, 517—520).—A large flock of sheep were fed with lupines, of which the seed contained 1 per cent. of alkaloids. In less than three weeks more than half of them died. The lupine hay was covered with a kind of fungus, but whether this had anything to do with its poisonous effects was not ascertained.

J. K. C.

**Disease in Sheep caused by Lupine.** By J. KÜHN (*Bied. Centr.*, 1880, 550—552).—As the injurious action of lupine seeds can be prevented by steaming, the author suggests that experiments be

instituted to find whether this result may be obtained by the overheating of lupine hay during its preparation. J. K. C.

**Composition of Two Varieties of Turnips.** By G. JANECEK (*Bied. Centr.*, 1880, 532—530).—Two kinds of turnips, "golden tankard" and "mammoth red long," were analysed; the former produced diarrhoea when given as fodder, and the cause of this was explained by the chemical constitution of the ash, which was found to contain more soluble nitrates and sulphates than the former.

J. K. C.

**Value of Acorns as Fodder.** By H. CZUBATA (*Bied. Centr.*, 1880, 327—328).—The author's experiments with *Quercus pedunculata* and *Q. cerris* shows that the kernel of the acorn is a valuable food when supplemented by starchy material; nearly half the husks consists of cellulose. He states also that the kernels of various species of oak differ considerably in the proportion of their constituents.

The chemical analyses of the two above-named varieties will give a fair idea of the general composition of the kernels:—

*Soluble Constituents—per cent.*

|                             | Sugar. | Dextrin. | Protein. | Ash. | Other organic matter. |
|-----------------------------|--------|----------|----------|------|-----------------------|
| <i>Quer. ped.</i> . . . .   | 3.31   | 0.0      | 1.21     | 2.70 | 11.82                 |
| <i>Quer. cerris</i> . . . . | 6.71   | 4.72     | 0.62     | 1.99 | 7.97                  |

*Insoluble Constituents—per cent.*

|                         | Cellulose. | Oil   | Ash. | Protein. | Starch. | Other organic matter. |
|-------------------------|------------|-------|------|----------|---------|-----------------------|
| <i>Quer. ped.</i> . .   | 1.95       | 6.03  | 0.10 | 4.82     | 64.48   | 5.01                  |
| <i>Quer. cerris</i> . . | 2.51       | 11.52 | 0.20 | 3.52     | 58.54   | 1.60                  |

J. F.

**Cultivation of Sugar-beets.** By A. LADUREAU (*Bied. Centr.*, 1880, 321—326).—This paper is a report of experiments made at the Agricultural Experimental Station of the Department du Nord in the year 1878, on the culture of the sugar-beet. The experiments were divided into four sections: firstly, as to the effect of increased quantities of suitable manures; secondly, a comparison of the effects of twenty different manures; thirdly, the sowing of sprouted or unsprouted seeds; fourthly, on the advantages of ridge culture. The first experiment was made with a mixture of manures which the author had previously found to be efficacious; it contained nitrogen in three forms, viz., in combination with organic substances, 2.60 per cent.; in the form of ammonia, 3.00 per cent.; as nitric acid, 2.25 per cent.; available phosphoric acid, 7 per cent.; potash, 5 per cent.; 100 kilos. of this manure cost 30 francs, and the quantities employed were 350, 700, 1,050, 1,400, 1,750 kilos. per hectare; one plot remained unmanured. The seeds were of two sorts; one the so-called Betterave de Pologne, and the other the acclimatised White Silesian. The field was a clayey soil; the seed sown on 30th April; the manure spread out some time previously. In one portion it was ploughed in, while in the other it was laid in the furrow.



The results were tabulated, and the following conclusions drawn by the author:—The weight of the crop increases proportionally to the manure employed. The ploughing in of the manure invariably produced better crops than when left in the furrows.

At an examination made 1st September of roots taken from plots treated with the larger quantities of manure, the juice was thinner and poorer in sugar; but after that, the differences equalised themselves. The actual quantity of sugar yielded increased with the increase of manure. With similar quantities of manure, the red-topped beet produced heavier roots and more sugar, but the juice of the white Silesian was richer in sugar. With both kinds of seed the results of the experiments were very satisfactory, there being an increase in the crop more than sufficient to compensate for the expense incurred.

The manner of distributing the manure has also a considerable effect on the *form* of the roots. The plants grown on the plot which had been ploughed in were regularly formed; only 25 per cent. with side roots or any irregularities, whilst 60 per cent. of the roots from the other plots were irregular, forked, and side-rooted.

The experiments on the effect of different manures were made on soil of a medium quality; a cold, damp, clay field, poor in lime. Sowings made 1st June; digging out on 5th October; on 1st September an examination of the roots was fairly made. In respect of weight, the later drawn roots had the advantage over the earlier; the easily decomposed salts were assimilated in the earlier portion of the time. During the last month of the period, very little change took place in the quantity of juice or its sugar contents.

There were 25 sorts of manure tried, and the author, as in the former case, summarises the results of his tables thus:—The addition of precipitated phosphate to stable manure gave no remarkable results. Superphosphate was better, but not more than lime alone, which goes to prove that the soil was deficient in lime rather than in phosphoric acid. Wool waste and rags gave their best results when mixed with caustic solutions and rendered soluble; the addition of lime increased the amount of the crop considerably; phosphoric acid and potassium superphosphate had a similar effect. The best results were, however, obtained when chemical manures were ploughed in together with lime; lime in combination with roasted leather also produced good results. Slaked lime in powder is more efficacious than unslaked in lumps. Sodium nitrate, particularly mixed with lime, gave higher results than ammonium sulphate.

These experiments are considered as proving conclusively the advantage of employing manure containing nitrogen in the three forms already referred to, with the addition of available phosphoric acid and potash.

The employment of seeds sprouted, according to Derôme's method, was the subject of the next experiment. The seeds, after being steeped, are allowed to heat spontaneously until the germination is started. So prepared, they appear above ground in four or five days at latest, and grow very regularly; the start which they get saves them from the insects to which they are liable to become a prey when tender. A bottom layer of chemical manure under the seeds about

$\frac{1}{2}$  to  $1\frac{1}{2}$  cm. deep helps their progress. Ladureau's experiments with nine different sorts of manure bears out Derôme's conclusions as to the decided advantage of sowing the sprouted seeds. J. F.

**Potato Culture.** By P. WAGNER and W. ROHN (*Bied. Centr.*, 1880, 339—341).—The design of the authors was, by an extensive series of experiments with different varieties of the root, to discover the particular kind most suitable to the soil and climate of their province; for this purpose they selected 75 different kinds of potato, and, having carefully cultivated them, give the results in gross weight and percentage of starch, of which the following are those obtained with a few of the most prolific sorts. The third column shows the relative yield as compared with the average of the whole 75 taken as 100. The morgen equals 0.25 hectare, the centner 50 kilos:—

| Sorts.                       | Centner per morgen. | Starch per cent. | Comparative yield. |
|------------------------------|---------------------|------------------|--------------------|
| Red Aldekerte.....           | 136.8               | 18.4             | 153                |
| White Bavarian .....         | 123.6               | 16.1             | 138                |
| Patterson's Elegancy .....   | 140.0               | 17.2             | 156                |
| Richter's Imperator.....     | 241.1               | 19.8             | 269                |
| Patterson's Blue Irish. .... | 125.1               | 17.1             | 140                |
| Irlachin.....                | 161.0               | 15.2             | 180                |
| Richter's Snowrose .....     | 159.5               | 16.4             | 178                |
| Early Vermont.....           | 132.4               | 16.3             | 148                |
| Violet Victoria.....         | 165.6               | 19.2             | 184                |

The astonishing results of Richter's imperator strike the eye at once, and every one who has cultivated it agrees that it is of a very hardy nature; it is also a handsome, smooth potato, and the stalk strong and straight. The authors recommend this variety most strongly to the attention of farmers; the other sorts mentioned are also commended. J. F.

**Damage to Pea and Bean Seeds by Weevil.** By E. WOLLNY and others (*Bied. Centr.*, 1880, 341—343).—The authors refer to previous experiments by G. Marck, already noticed (this vol., p. 734), in which he says that the larvæ of this beetle generally destroy both plumula and radicula; and they say that such destruction is quite exceptional, but that beans suffer less than peas. The result of twenty experiments prove the damaged seeds to be slower in their germination, and the young plants weaker than those from untouched seeds. The yield from the sound seeds was also greater than from the unsound.

It is recommended to suspend the cultivation of these crops for several years when the weevils appear to have made their home in any part of the farm. The means recommended for destruction of the pest is the use of carbon bisulphide vapour in close vessels, where they perish in less than ten minutes.

Further examinations of the seeds showed that 100 contained 190—200 larvæ, some of them having as many as six in the one seed.

J. F.

**Cultivation of Beet Seeds.** By K. MÜLLER (*Bied. Centr.*, 1880, 381).—This is a report of comparative trials of the qualities of certain beet seeds raised by Simon Legrand, a famous French seed grower. The experiments were made against certain favourite local sorts; they resulted entirely in favour of M. Legrand's seeds, but the details are not of general interest.

J. F.

**Analysis of Beet Seed.** By H. PELLER and M. LIEBSCHUTZ (*Compt. rend.*, 90, 1363—1365).—Four sorts of seeds were taken for examination:—(1.) Red-crowned white sugar-beet. (2.) Improved white "vilmorin." (3.) Green-crowned beet. (4.) Red variety. 100 seeds weighed 2.083 grams. The seeds were rubbed between two wire sieves so as to separate the exterior portion called *dentelle* or envelope, from the interior portion or nucleus, in order that both might be analysed separately. 100 grams of seed yielded 14.87 grams of envelope and 85.13 grams of nucleus (*vide* Table, p. 921).

The quantity of mineral matter contained in the envelope is nearly three times as great as that in the nucleus, whilst the latter is richer in fatty substances and starch.

The authors propose to keep some seeds for three or four years in order to ascertain whether the oxidation of the fatty matter is the cause of its non-germination, it having been stated by Ladureau, more especially in connection with oleaginous seeds, that this is the cause of the non-germination of old seeds.

J. W.

**Investigation of the Composition of Soil from a Graveyard.** By E. REICHHARDT (*Arch. Pharm.* [3], 15, 421—426).—The graveyard from which the samples were taken had been unused for thirty years, and they were taken in two series from depths of (1) 2 metres; (2) 1½ metre; (3) 1 metre; (4) 0.5 metre below the surface; (5) the surface. In none of them could ammonia be detected, and they lost when ignited quantities varying from 5.1—8.7 per cent. of their weight; part of this loss must be due to carbonic anhydride, as the soil consisted principally of dolomitic chalk. Ignited with soda-lime, the samples from the surface yielded larger quantities (0.28) of nitrogen than the samples from 2 metres (0.14). Also when ignited in closed tubes it was found that all samples yielded water, ammonia, and animal oil, but that this was yielded in larger quantities by the surface than by the lower soil.

E. W. P.

**Influence of the Soil on the Tannin of Oak-bark.** By M. FLEISCHER (*Bied. Centr.*, 1880, 489—491).—In order to compare the quantity of tannin in the bark of oak trees grown on sandy soil and moorland, samples of the bark of ten twelve-year old trees grown on each of the two kinds of soil were taken and analysed; bark of oak from sandy soil was found to contain 4.3 per cent., and that from moorland 5.7 per cent. of tannin.

J. K. C.

*Composition of Beet-seed.*

|  | Envelope.   |           | Nucleus.    |               | Normal seed. |           |
|--|-------------|-----------|-------------|---------------|--------------|-----------|
|  | Percentage. |           | Percentage. |               | Percentage.  |           |
|  |             | Nitrogen. |             | Ash per cent. |              | Nitrogen. |
| Water .....                                | 14·000      | —         | 11·000      | —             | 11·446       | —         |
| Silica .....                               | 4·869       | —         | 0·142       | 2·600         | 0·845        | —         |
| Phosphoric acid .....                      | 0·840       | —         | 0·898       | 16·410        | 0·815        | —         |
| Sulphuric acid .....                       | 0·596       | —         | 0·225       | 4·120         | 0·280        | —         |
| Chlorine .....                             | 0·283       | —         | 0·147       | 2·695         | 0·167        | —         |
| Potash .....                               | 2·690       | —         | 1·020       | 18·617        | 1·268        | —         |
| Soda .....                                 | 1·267       | —         | 0·550       | 10·047        | 0·657        | —         |
| Lime .....                                 | 2·080       | —         | 1·180       | 21·580        | 1·315        | —         |
| Magnesia .....                             | 2·844       | —         | 0·703       | 12·838        | 0·947        | —         |
| Nitric acid .....                          | 0·063       | 0·016     | traces      | —             | 0·069        | 0·002     |
| Ammonia .....                              | 0·184       | 0·111     | 0·103       | —             | 0·108        | 0·089     |
| Nitrogenous substances (coagulable) .....  | 9·420       | 1·507     | 8·230       | —             | 8·406        | 1·845     |
| Fatty and colouring matters .....          | 2·000       | —         | 5·536       | —             | 5·010        | —         |
| Starch .....                               | 13·729      | —         | 18·071      | —             | 17·425       | —         |
| Cellulose .....                            | 26·000      | —         | 20·880      | —             | 21·600       | —         |
| Soluble proteids .....                     | 8·760       | 0·800     | 4·293       | —             | 4·211        | 0·665     |
| Undetermined substances .....              | 16·468      | —         | 27·105      | —             | 26·526       | —         |
| Carbonic anhydride .....                   | —           | —         | —           | 11·750        | —            | —         |
| Total .....                                | 100·063     | 2·234     | 100·038     | 100·607       | 100·085      | 2·101     |
| Deduct oxygen equivalent to chlorine ..... | 0·063       | —         | 0·033       | 0·607         | 0·085        | —         |
|  | 100·000     | —         | 100·000     | 100·000       | 100·000      | —         |

**Ash of Beet.** By H. PELLET (*Bied. Centr.*, 1880, 529—532).—For every 100 kilos. of sugar in beet about 13 or 14 kilos. of ash, consisting chiefly of alkaline and earthy phosphates, are taken up from the soil.  
J. K. C.

**Experiments on the Growth of Hyacinths.** By A. E. v. ROGEN (*Bied. Centr.*, 1880, 381).

**Sowing Broadcast or in Drills.** By PAETOW (*Bied. Centr.*, 1880, 374—375).—Two plots of ground were well tilled 12 inches deep, and one of them sown broadcast with rape; the other plot was sown in drills, the former very thinly; frost came on in May which did this plot some slight damage, the stalks in the drills were stronger, and, consequently, did not suffer so much; the yield per 100 square ruten was—

|                                      |            |
|--------------------------------------|------------|
| The portion sown in drills.....      | 251 kilos. |
| Broadcast .....                      | 207 „      |
|                                      | <hr/>      |
| Surplus in favour of drill culture.. | 42 „       |

J. F.

**Manuring Experiments.** By P. WAGNER and G. DRECHSLER (*Bied. Centr.*, 1880, 491—499).—Manuring experiments carried out by different individuals have yielded such varying and often conflicting results, that it has been proposed to allow a working error of  $\pm 5$  per cent. in each experiment; if this, however, were fully carried out, the variety and conflicting nature of the results would be very largely increased, instead of diminished. The only method of obtaining genuine comparative results is to take great care that the conditions of each experiment should vary as little as possible. Wagner makes use of small plots of land, from 1 to 2 meters square, separated by walls of cement, containing soil which has been made as uniform as possible in quality by careful mixing, and six plots, at some distance from each other, are selected for each kind of manure to be operated on. By this means the experimental error may be reduced to 1 per cent. Drechsler recommends that, as soils are nowhere uniform, experiments with the various crops to be raised should first be carried on without any manure, in order to ascertain the capabilities of the soil of the various plots used, and to make allowance for these in interpreting the results of manuring experiments.  
J. K. C.

**Manuring Experiments with Wheat.** By P. GENAY (*Bied. Centr.*, 1880, 372).—The following experiments on the effect of different manures on wheat are of interest; but the author expressly says that the results are only of decisive value for his own land. The ground had not been manured for the previous three years.

| Name of manure.       | Amount applied per hectare. | Crop.  |        | Gain over unmanured. |        |
|-----------------------|-----------------------------|--------|--------|----------------------|--------|
|                       |                             | Grain. | Straw. | Grain.               | Straw. |
|                       |                             | kilos. | kilos. | kilos.               | kilos. |
| Chili saltpetre ..... | 200 kilos....               | 2150   | 5040   | 550                  | 1160   |
| Poudrette .....       | 25 hlitters. . .            | 2000   | 4960   | 400                  | 1040   |
| Malt combings .....   | 1000 kilos. . .             | 1950   | 4800   | 350                  | 740    |
| Poppy cake .....      | 600 kilos. . .              | 1900   | 4720   | 300                  | 880    |
| Chili saltpetre ..... | 100 kilos. . .              | 1900   | 4560   | 300                  | 640    |
| Poudrette .....       | 15 hlitters. . .            | 1850   | 4720   | 250                  | 840    |
| Do. ....              | 33 „ . .                    | 1800   | 4960   | 200                  | 1040   |
| Unmanured .....       | —                           | 1600   | 3880   | —                    | —      |

J. F.

**Manuring Experiments on Moorland.** By WALDNER and STAUBESAND (*Bied. Centr.*, 1880, 499—500).—Bone-meal and potash salts were employed as the manures. Two plots of moorland, one uncultivated and the other reclaimed, were separated each into two parts, over one of which sand was strewn to the depth of 2 cm., and planted with potatoes. The yield was not satisfactory in any case, but the plots which had been covered with sand produced much more than the uncovered soil, especially where potash salts were employed as manure.

J. K. C.

**Manuring Experiments with Beet-sugar.** By M. MÄCKER (*Bied. Centr.*, 1880, 505—509).—In some cases Chili saltpetre gave better results when applied in autumn, and in others when used in spring; in combination with superphosphate, the best yield was obtained when the crops were manured in spring, whereas sulphate of ammonia applied in autumn always produced a better effect than in spring, although in neither case was the yield equal to that obtained by the use of Chili saltpetre in the early part of the year. The quality of the produce was very little influenced by the use of any manure except phosphate, the latter raising the percentage of sugar in the sap from 11·8 to 12·5, the results being most favourable when the phosphate was applied in spring.

J. K. C.

## Analytical Chemistry.

**Method for Determining the Temporary Hardness of Water.** By V. WARTHA (*Ber.*, 13, 1195—1198).—10 c.c. of the water are introduced into a cylinder graduated in cubic centimeters; to this is

added a piece of filter paper, which has been saturated with the extract of Campeachy wood and dried. To the water thus coloured, centinormal hydrochloric acid is added, until it becomes orange, and is then well shaken; the greater portion of carbonic acid is evolved, and the solution becomes red; acid is added, and the shaking repeated until the liquid assumes a bright orange yellow. The amount of hydrochloric acid added may be read off on the cylinder, and may either be calculated as calcium carbonate, or in degrees of alkalinity, which the author proposes should be done, since the alkalinity of a water depends not only on carbonates of calcium and magnesium, but also on alkaline carbonates and silicates. Every cubic centimeter of centinormal hydrochloric acid is taken as a degree of alkalinity. In some good waters, the author finds this to vary from 3–6°, whereas in bad waters it rises to 15°. This method is specially adapted for travellers, as it requires the use of very little apparatus.

When water is heated under pressure, its alkalinity decreases with increase of pressure.

P. P. B.

**Estimation of Retrograde Phosphoric Acid as Ammonium Citrate.** By A. KÖNIG (*Bied. Centr.*, 1880, 552–553).—By using quantities of the same material, varying from 0.5 to 2 grams, the percentage of phosphate dissolved in ammonium citrate was found to vary as much as 7 or 8 per cent., according to the proportions taken; results, therefore, obtained by this method can only be even comparative when the same quantity of material is used.

J. K. C.

**Standard Soda Solution.** By H. ENDEMANN and G. A. PROCHAZKA (*Chem. News*, 42, 8).—The authors confirm the statement of Gerresheim (*Annalen*, 1879) regarding the basic properties of Millon's base, obtained by the action of ammonia on mercuric oxide. Soda solution containing chlorine, sulphuric, silicic, and carbonic acid, may be freed from these impurities by shaking with the base. A chemically pure standard soda solution may also be prepared by this means.

L. T. O'S.

**Detection of Copper.** By H. ENDEMANN and G. A. PROCHAZKA (*Chem. News*, 42, 8).—On evaporating a solution of cupric bromide, its colour changes from blue to reddish-brown, and finally to black, the anhydrous bromide being formed. By adding concentrated hydrobromic acid to a dilute copper solution, a dark brownish-red or a violet colour is at once produced. 0.001 mgrm. of copper may readily be detected by this means.

L. T. O'S.

**A Lecture Experiment.** (*Chem. News*, 42, 27).—By means of Holman's lantern for the oxyhydrogen blowpipe, which may be used either as a vertical lantern, a projecting microscope, or a megascope, the cupellation of gold or silver may be effectively illustrated.

The cupel is held by means of a thick copper wire in the focus of the light from the condensing lenses of the lantern; its image is projected on the screen, and it is brought to incandescence by means

of the oxyhydrogen blowpipe. The weighed quantity of alloy, enclosed in sheet lead, is dropped into the cupel, whereby it is melted, and the lead as it is oxidised is absorbed by the cupel, forming a dark ring in the bottom. As the precious metal becomes exposed to view, a sheet of light passes over the surface, and finally, when all the lead is absorbed, the purified metal becomes visible as a brilliant globule.

L. T. O'S.

**Detection of Cotton-seed Oil in Olive Oil.** By B. NICKELLS (*Chem. News*, 42, 27).—Olive or Gallipoli oil gives an absorption-spectrum showing a cutting out of the blue and violet rays, a fine line in the green, and a distinct deep band in the red. Cotton seed oil gives the same result in the blue, but the green and red are continuous. By comparing the spectrum of the suspected oil with that of a standard thickness of olive oil, any difference in the intensities of the band in the green and red portions of the spectrum will indicate adulteration of the oil.

L. T. O'S.

**Stall Sampling in Milk Analysis.** By P. DU ROI and KIRCHNER (*Bied. Centr.*, 1880, 352—354).—The authors propose that when a suspected sample shows on the lactodensimeter an abnormally low degree, that a proper officer should milk the cows in the stall within one day at latest from the time of confiscating the original sample, the analysis of the second being made in exactly the same manner as the first sample.

This recommendation is based on the consideration that milk experiences very little alteration during 24 hours, either as regards specific gravity or composition, in support of which the authors give some comprehensive tables. From these tables, it may be seen that old milking cows yield a higher percentage of total solids and of fat than fresh milkers. The older milkers gave with two exceptions 13, 14, and even 16 per cent. total solids, and 4 to 5 per cent. butter; the young milkers giving seldom over 13 per cent. solids, and the butter ranged between 2·348 and 4·573 per cent. The milk of a herd when mixed together varies but little from day to day; but when a single cow is in question, there may be palpable differences between the morning and evening milkings, and the authors caution analysts against too speedy a condemnation on insufficient data. Tollens, commenting on this paper, recommends that analysts should cease to certify that milk is adulterated with such and such a percentage of water, but to fix a standard sufficiently high to condemn all milk below that, and have it sold at a low price, whilst milk which reached or passed the standard should be designated good, particularly good, nursery milk, &c., &c.: that in fact the quality should rule the price in the same way as choice joints of meat are charged a higher price than those which are coarser.

J. F.

**Milk Analysis.** By BEHREND and others (*Bied. Centr.*, 1880, 351—352).—The three data in milk analysis which are generally determined experimentally—fat, total solids, and sp. gr., are interdependent, and the authors formulate a method of deducing one of them when



the other two are known. The fat being determined by the lactobutyrometer, and the sp. gr. in the usual manner, the authors, by means of voluminous tables which they have compiled, determine the "solids not fat," and adding thereto the fat obtain the "total solids." They have submitted their tables to proof by analysing a number of samples and comparing the results with those shown in the tables, the difference being very small, not 0.38 per cent. Clausnitzer and Mayer determine the sp. gr. and obtain the total solids by evaporating 0.5 c.c. in a platinum capsule at 110° in a drying chamber with glass doors and cover, and obtain the fat by the following formula:—

$$X = t \times 0.789 - \frac{S - 1}{0.00475}.$$

X being the fat sought,  $t$  the total solids found,  $S$  = sp. gr. of the milk: for example—

$$12.70 \times 0.789 - \frac{1.0325 - 1}{0.00475} = 3.18 \text{ per cent. fat sought.}$$

One of the authors made an attempt to estimate the water in milk by means of common salt, the principle being the same as that employed in beer analysis, where the poorer the beer in alcohol, the more salt it will take up. This succeeded with the milk to a certain extent, but eventually it became so thick that the sp. gr. could not be taken, and the attempt was abandoned as unsuccessful. J. F.

**Condensed Milk.** By E. WEIN (*Bied. Centr.*, 1880, 362).—Experiments have shown the author that the fat in condensed milk cannot be estimated in the usual manner by evaporation with sand and treatment in an ether apparatus, as the large quantity of sugar present causes the formation of hard lumps which the ether cannot penetrate.

The method he pursues is to place 5 grams of the milk in a dish and treat it with continually renewed quantities of ether until it is all washed through a filter into a flask; sea-sand is added, and the lumps which form constantly broken up, and the operation repeated until all the fat is completely exhausted; the ether evaporated, the fat redissolved, the ether again evaporated, and the fat weighed. For the nitrogen determination, the author adds gypsum, dries on the water-bath, and proceeds according to the soda-lime process: if the milk be dried in Hoffmeister's dishes, care must be taken not to employ too great heat as a small loss of nitrogen occurs, 0.2 per cent. Some samples of condensed milk made in a certain factory, examined according to this method, gave results very close to those obtained with normal milk.

J. F.

**On Blood Stains.** By D. VITALI (*Gazzetta*, 10, 213—225, and 261—264).—The author points out that the blue colour produced when a mixture of turpentine and alcoholic solution of guaiacum is agitated with blood, is an effect of oxidation, and may readily be produced by many other substances, especially if copper or iron salts are present. It is necessary therefore to use this test with great caution: the suspected fluids should first be agitated with a small quantity of tincture of guaiacum and allowed to stand some hours, when it will

remain colourless if no substance is present capable by itself of colouring the guaiacum. If, however, blood is present, a blue colour will be produced on adding turpentine to the mixture and agitating. If the stains have dried, they should be dissolved off with a little dilute solution of potash free from nitrites, and the liquid neutralised with acetic acid previous to adding the tincture of guaiacum. The author has observed that the guaiacum, when precipitated from its alcoholic solution by water in presence of hæmoglobin, carries down the whole of the latter, so that the test becomes one of extreme delicacy, the reaction being quite distinct with a solution containing one part of dried blood in one hundred millions, especially if it is gently heated. The precipitated resin, however, is in so fine a state of division that it is very difficult to collect it, and it is better to agitate with ether or amylic alcohol. With the former, the blue colour is produced at once in the cold without the addition of turpentine; with the latter, heat must be applied. It was found that the colour reaction was obtained even with dilute blood which had been allowed to stand two months in an open vessel and had become putrid. C. E. G.

**Colouring-matter of Grapes and Bilberries and the Artificial Colouring of Red Wines.** By A. ANDRÉE (*Arch. Pharm.* [3], 16, 90—112).—The results of the author's researches on wine prepared by himself from Bordeaux grapes are (1) the colouring-matter does not vary with the different grapes, and this colouring-matter is removed from the skins during fermentation by the tannin acid, the colour being blue or red according to the amount of acid present. (2) The blue colouring-matter is unaltered in its composition by fermentation; but a wine by keeping becomes paler in colour because of the precipitation of the colouring-matter caused by the decomposition of the tannin which holds this substance in solution. (3) The tint is no criterion whereby to judge of the presence of fermented bilberry juice, the test being solely dependent on the amount of acid present, for as wine becomes brown by age, so does bilberry juice. It has been stated that an unadulterated wine will not produce a coloured foam, but this is incorrect, as all young wines when shaken do produce a coloured foam, a foam dependent for its quantity on the amount of tannin present, but for its permanency on the alcohol, and disappearing more quickly the more highly alcoholic the wine. Reactions with wine should be carried out in a shallow white porcelain basin, 5—10 grams only of the wine being employed, and the resulting colours observed by reflected light; and then if the reactions are different from what was expected, the difference is due, not to the colouring-matter, but to the substances which are present in the wine in varying proportions. In a series of experiments it is shown that ammonia changes the colouring-matter of wine or bilberries, which is naturally of a rose or lilac tint, to a blue, which with excess of ammonia becomes colourless; an intermediate tint of green may also be observed; this green colouration may sometimes amount to a precipitate, which seems to be a compound of ammonia and the colouring substance. In the case of an old wine, the green precipitation occurs immediately on addition of the ammonia,

but rapidly changes to a brown; this reaction is exactly the same as that which occurs when the bilberry colouring-matter is substituted for the wine. Ammonium, sodium, and potassium hydrates and carbonates react in a similar way, no difference between the two colouring materials being observable.

Upon one test, great reliance has heretofore been placed, because of the great delicacy which it possesses for the detection of minute traces of bilberry colouring-matter. When burnt magnesia is worked up into paste with water, placed in a shallow basin, and then wine poured on the surface of the magnesia, the magnesia is tinted blue-grey or blue-green (according as the wine is coloured blue or green by ammonia), which tint rapidly changes to a grey-brown or brown; whereas with bilberry the colour is blue, and with mallow green. The author has found that all commercial wines are identical as regards the above reaction, but finds that with wine which he has himself prepared, the colours produced are identical with that of the bilberry; hence he concludes that this test must no longer be considered to be of value. Several other tests are tried, and the conclusion drawn is, that, *cæteris paribus*, there is no distinction between the colouring-matters in either the grape or the bilberry, but that often a distinction has been apparently discovered which, on careful examination, may be shown to be due to other substances present in the bilberry extract, as for example, the precipitate formed by lead acetate in a wine is finely divided, whereas when bilberry juice is employed the precipitate is coarse; but if the alcoholic extract of the berries is used, the two precipitates are identical in appearance; the difference is shown to be due to the pectin in the aqueous extract. The final result then of the investigation is, that the two colouring-matters are identical. They have been prepared by treating the lead precipitate with sulphuretted hydrogen, and then digesting the mass with alcohol and acetic acid; as long as acid is present, the solution is red, but when all acid has been evaporated, the solid is of an indigo-blue. It is completely insoluble in alcohol and ether, but only when all acid is absent.

E. W. P.

**Determination of Wine-extract.** By E. A. GRETE (*Ber.*, 13, 1171—1175).—For this purpose the author proposes to evaporate 10 c.c. of the wine with 10—20 c.c. of titrated baryta-solution; the residue obtained is heated at 110° until its weight is constant. The residue consists of the barium salts of the acids present and of a molecular compound of barium oxide and extract constituents and of barium carbonate. To ascertain the amount of baryta used to form salts, 10 c.c. of the wine are titrated with baryta-solution: for every molecule of  $\text{Ba}(\text{OH})_2$  used,  $\text{Ba} + \text{H}_2$  must be deducted from the weighed residue. The amount of barium oxide is determined by dissolving the residue in water and titrating with sulphuric acid. The sum of the c.c. of baryta corresponding with this, and those needed to neutralise the acids, when deducted from the number of c.c. taken, give the number of c.c. of baryta which have been changed into carbonate. The sum of the weights of barium carbonate, oxide, and  $\text{Ba} + \text{H}_2$ , when deducted from the weight of total residue, gives the weight of extract required.

P. P. B.

**Malt Examination.** By J. S. LIPPS (*Bied. Centr.*, 1880, 383).—This paper describes the behaviour of a certain reagent employed by the author in malt examinations. He describes it as a basic lead acetate, which is not to be confounded with "Goulard's solution;" but there are no details as to its preparation, although some description of its reactions is afforded. The principal advantage in its employment appears to be that when added to a cold solution containing dextrin and starch, the latter is precipitated, and when the solution is boiled, the former thus affording an easy means for separating and estimating the two. J. F.

**Detection of Oiled Wheat.** By C. HIMLY (*Bied. Centr.*, 1880, 389).—The author has devised a simple method of detecting this sophistication, which appears preferable to others commonly employed. A sample of the suspected wheat is shaken up in a perfectly clean flask with some of the bronze powder ordinarily used in printing illustrated tickets, &c., and it is then emptied on a clean dry filter-paper, and rubbed with it; the oiled grain will hold the powder and present a fine gilt appearance; if the grain has not been oiled, the bronze-powder will not adhere. J. F.

## Technical Chemistry.

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**Silver Bromide Gelatin Emulsion.** By T. SCHNAUSS (*Arch. Pharm.* [3], 16, 113—116).—A short history of the introduction of the emulsion process for photography occupies the first portion of the article, and is followed by the following receipt, which is used with success at the observatory in Potsdam:—In an opaque flask 1·6 gram of ammonium bromide is dissolved in 40 c.c. of distilled water, and to this is added 4·6 grams of Nelson's gelatin; after an hour the flask is placed in warm water so as to melt the mass, and 2·52 grams of silver nitrate dissolved in 17 c.c. of distilled water are added, and the whole well shaken. To attain the highest sensitiveness, the emulsion is kept at a temperature of 30° for several days; afterwards nothing more is required than to wash the emulsion free from ammonium bromide and nitrate. When thoroughly washed the emulsion is melted, poured on to horizontal glass plates, and dried over calcium chloride or sulphuric acid; when dried, the plates are piled one on the other, but kept separate by pieces of tissue-paper; naturally all these operations must be conducted in non-actinic light. The "developer" employed is either "pyro" containing ammonium bromide, and made alkaline by ammonia, or a concentrated solution of ferrous oxalate dissolved in potassium oxalate. E. W. P.

**Disinfection and Preservation of Animal Matters, such as Blood, for Agricultural Purposes.** By E. VAUTELET (*Compt. rend.*, 90, 1365).—The process consists in the use of the following sub-

stances in proper proportions:—(1) Aluminium sulphate. (2) Sulphuric acid. (3) Nitric acid. By the addition of sulphuric acid to aluminium sulphate, an acid sulphate is formed; this salt, less soluble than the neutral one, when added to blood causes its rapid coagulation. Nitric acid may be used with similar effect. No details are given.

J. W.

**Purification of Water from Sugar Works.** By W. KNAUER and others (*Bied. Centr.*, 1880, 537—539).—After filtration through a sieve, Knauer recommends heating the water by means of steam to  $81^{\circ}$ , treating with milk of lime, and then with manganese chloride; after the deposits have settled, the water is cooled and allowed to run off through a sieve. This method was investigated by a commission, but was not considered satisfactory. Tölke limits the consumption of water, and then drains it off through soil.

J. K. C.

**Malleable Nickel.** By J. GARNIER (*Compt. rend.*, 90, 331—333).—By adding to pure nickel, which after fusion is brittle, some substance which will readily combine with the oxygen absorbed by the molten metal whilst cooling, and which will diffuse through the whole mass, it may be made perfectly malleable. Phosphorus is best adapted for this purpose, 0.3 per cent. being sufficient to render the nickel soft and malleable, a greater quantity of phosphorus makes the metal harder and less malleable. The phosphorus is added in the form of phosphide of nickel, containing about 6 per cent. of phosphorus. It is prepared by fusing a mixture of calcium phosphate, silica, charcoal, and nickel. Nickel containing 0.25 per cent. of phosphorus may easily be rolled into leaves 0.5 mm. thick. L. T. O'S.

**Mercuric Oxide in Grey Powder.** By D. LINDO (*Chem. News*, 42, 67).—Grey powder, after keeping for some time, is found to contain large quantities of mercuric oxide, and therefore becomes unsuitable for medicinal purposes.

L. T. O'S.

**Strong's Water Gas System.** By G. S. DWIGHT (*Chem. News*, 42, 27—29).—This system consists in raising coke to incandescence and causing the products of combustion to superheat a given quantity of steam, which is brought into contact with coal-dust, and then led back to the coke. In this way it is possible to utilise all the heat evolved in the combustion of coal, to within 10 or 12 per cent. of the theoretical value.

Experimental and numerical details are given in the paper.

L. T. O'S.

**Vaseline.** By H. WERNER (*Arch. Pharm.* [3], 16, 45).—Three samples of vaseline of German, Austrian, and American origin were examined, and appeared to behave differently when mixed with balsam of Peru, although of the same general appearance. The German and Viennese samples mixed completely to half their weight in the balsam, whereas the American sample mixed completely with its own weight of the balsam, and did not separate even on standing for a considerable time.

E. W. P.

**Purification of Spirit.** By J. E. BERLIEN (*Bied. Centr.*, 1880, 543—544).—A small quantity of solution of silver nitrate removes all unpleasant aroma from the crudest spirit of commerce. J. K. C.

**Fermentation of Molasses.** By M. FIEDLER (*Bied. Centr.*, 1880, 545—545).—Molasses which had been kept a long while and was in a condition highly unfavourable to fermentation, was subjected to two different methods of treatment; in one case the molasses was diluted and boiled with a small quantity of sulphuric acid, again diluted and allowed to ferment, the yield of alcohol being 84 per cent. of the theoretical amount: in the second experiment the molasses was carefully neutralised with chalk, diluted, and then allowed to ferment, 90 per cent. of the theoretical yield being obtained. J. K. C.

**Fermentation of Beet-root Sap obtained by Diffusion.** By A. MILLOT and MAQUENNE (*Bied. Centr.*, 1880, 560).—An inflammable gas is given off by this sap after fermenting for some time; this the authors have explained by showing that butyric fermentation sets in, causing hydrogen to be evolved. J. K. C.

**Aeration of Must.** By E. ROTONDI (*Bied. Centr.*, 1880, 545—546).—By passing air through must, the ferment is more thoroughly mixed with the liquid, and the decomposition of sugar and albumin becomes more rapid. Wines which have been prepared in this manner age more quickly, and are less liable to decomposition than other wines. J. K. C.

**Direct Decomposition of Sugar-lime.** By M. PAULY (*Bied. Centr.*, 1880, 559—560).—The author decomposes sugar-lime by means of carbonic anhydride, and obtains 96 per cent. of the calculated amount of sugar. J. K. C.

**New Clarifier for Beer.** By V. GRIESMEYER (*Bied. Centr.*, 1880, 386).—The *Baja clarata* has been recommended as a clarifier in breweries by Griesmeyer, and a great reduction in its price has brought it into considerable prominence recently. A brewer named Kubiak, in Ossegg, has made a series of experiments on its use, which he has published in several technical journals. He finds it a specific against muddiness in the yeast, that it causes a separation of the yeast at the top instead of the bottom of the cask, and that it is forced from the bung, requiring some little attention in this regard. J. F.

**Sap-quotient of Beet.** By F. SACHS (*Bied. Centr.*, 1880, 534—536).—The sap-quotient is defined as the number obtained by dividing the percentage of sugar in the root by the percentage in the liquid pressed out at the first pressing. In the author's experiment, the number was 0.94. J. K. C.

**Preparation of Sugar from Sap of Beetroots.** By K. LÖNN. (*Bied. Centr.*, 1880, 533—534).—The colouring-matter is separated by the addition of gelatinous alumina and gently warming: the sugar is obtained from the filtrate by crystallisation. J. K. C.

**Sorghum Saccharatum.** By A. v. WACHTEL (*Bied. Centr.*, 1880, 344—345).—This plant is extensively cultivated in certain parts of the United States for the manufacture of cane-sugar. It grows to a height of 12—14 feet in those regions, yields about 19,500 kilos. per Prussian morgen (0·25 ha.), and contains 10 per cent. of sugar. In the year 1850, an attempt was made to obtain spirit from it at Konigsaal, and an excellent rum was produced. In 1879 an attempt at cultivation was made at Czakowitz, in Bohemia, with American seed, and the plants were submitted to the author. They only attained a height of 5½ to 6 feet. The yield of cane-sugar was 15·3 per cent., and inverted sugar 0·85 per cent. The quantity of juice was small, and the waste about three times as great as from sugar-beets; the sap, however, appeared tolerably clear; the watery extract at 50° when concentrated produces a considerable crop of crystals, which became tolerably bright when washed with water. J. F.

**Sugar in Raisins.** By HAAS (*Bied. Centr.*, 1880, 386).—This paper gives an estimation of the contents in sugar of different sorts of raisins, varying from 14·5 to 61·75 per cent., and the observer cautions purchasers against buying on mere appearance when such material differences exist. J. F.

**Production of Sugar from Starch.** By RÖHR (*Bied. Centr.*, 1880, 547—548).—Temperatures varying from 40° to 52° R. have been recommended as the best for the production of sugar from potato-mash, and the time allowed from twenty minutes to two hours. The author finds that at any temperature between the above limits the conversion of starch into sugar is complete, and proposes as the most convenient digestion at a temperature of 44—46° R. for 1½ to 1½ hours. J. K. C.

**Preservation of Butter.** By H. BAY (*Bied. Centr.*, 1880, 388).—The experiments here recorded were made by Manetti, and show that butter thoroughly washed until the wash-water runs away perfectly clear, keeps sweet nearly twice as long as that which has been washed a shorter time and then packed. The addition of one-thousandth part of common salt preserves butter ten days, two-thousandths twenty days, and three-thousandths thirty days. The smaller quantity leaves a scarcely perceptible taste. The addition of one- to two-thousandths of borax preserves the butter 15 to 20 days. The flavour, however, is unpleasant. J. F.

**Whole Milk Butter Compared with Cream Butter.** By M. SCHRODT and P. DE ROI (*Bied. Centr.*, 1880, 363).—The author took equal quantities of the same milk, allowed them to cream; one of them he skimmed after 36 hours and churned the cream; the other portion he allowed to stand for 34 hours, when it became slightly acid. He churned the whole of it without skimming. The cream churned in 25—55 minutes; the whole milk took 35—65 minutes. The butter was weighed after the first kneading, unsalted, and the quantity of milk required to make a kilogram of butter calcu-

lated. The following are the averages of ten experiments in each case: whole milk, 28·76; cream, 30·35 of milk. The larger yield of the former is attributed to the presence of greater quantities of casein, milk-sugar, and water than in the cream butter, which naturally deteriorates its keeping qualities. J. F.

**Experiments with Laval's Separator.** By N. ENGSTRÖM (*Bied. Centr.*, 1880, 360—361).—In these experiments, the author was able to obtain 20 per cent. of cream, and compared with the Swart's method tried on milk of the same cows, the average surplus was 5·15 per cent., and even much more was obtained in certain localities. A prejudice exists against the butter made by this method as not being good for keeping, but the handling of the butter appears to have a great deal to do with it. When it comes from the separator the author puts the cream into ice-water, where it is left for 6—10 hours; it has then a clean fresh taste. It is warmed to 13° C., acidified, and in twelve hours churned at a temperature of 11°. By this method a butter is obtained which the most experienced butter dealers have classed in the first rank.

The refuse which collects in the outer division of the apparatus consists principally of organic matter free from fat. On being microscopically examined, it was found to contain, besides nuclein, portions of epidermic scales, a few fat globules, threads, &c. J. F.

**A New Skimming Process.** By A. MAYER and F. CLAUSNITZER (*Bied. Centr.*, 1880, 358—359).—The authors treat the milk with a small quantity of soda-solution, and find that it preserves the milk from decomposition from three to five days, and further, that it assists the separation of the cream, and leaves less fat in the skim-milk than the ordinary treatment. 1·3 to 1·5 grams of  $\text{Na}_2\text{O}$  to the kilogram of milk gives the best results; a larger quantity makes the casein so thick that creaming ceases. The quantity of cream taken off by this method being larger, the *percentage* of fat in it is naturally smaller than when a lesser quantity is removed; but the authors rely on the small quantity of fat left in the skim-milk as a proof of the completeness of the process.

An experiment was then made as to the quantity and quality of the cream so separated. Two of Swart's apparatus were prepared; in one was placed 15 litres of milk without soda, in the other the same quantity with 0·14 per cent. of  $\text{Na}_2\text{O}$ . After four days they were both skimmed, with the result that the portion treated with soda gave 669 grams of butter, and that without the soda 627 grams. The original percentage of fat in the milk was 2·32; the percentage obtained by the soda process was 1·83, and by the ordinary means 1·67. The butter was washed and worked. No disagreeable taste was perceived. It was kept in a cellar for several weeks, and was perfectly fresh at the end of that time. The skim-milk is, however, unfit for human food, owing to the strong taste of soda; after neutralisation, however, it can be used for pig-feeding. The reason of the process the authors are unable to give, but they think that the coating of



serum is attacked by the alkali, and the fat globules are liberated more freely. J. F.

**Experiments with Skimming by the Schwartz and Holstein Systems.** By M. SCHRÖDT and C. DU ROI (*Bied. Centr.*, 1880, 356—357).—Complaints are common of so-called "lazy milk," in which the cream does not separate well, and although good, does not yield its butter freely. The time of these complaints is generally about the period when the cows are put out first on the meadows, and it occurred to the authors that the sudden change from the dry hard feeding of the stalls to the tender soft grass had something to do with the cause of the complaint. They therefore caused a herd to be fed in the stalls with green food previous to being out at grass, commencing with small quantities of green fodder, and increasing it until they had nothing else. The experiment lasted 14 days, and at its end the cows were put out to grass, but there were no complaints of lazy milk.

The milk was divided into two portions, and separated by the Schwartz and Holstein methods. By the former it required 30.72 kilos. of milk to produce 1 kilo. of butter; by the Holstein method it only required 27.95 kilos. to yield the same quantity.

The meadowing of the cows had a great effect on the yield of butter, and while at grass the two systems gave almost identical results. J. F.

**Composition of Curds.** By M. RUBNER (*Zeits. f. Biologie*, 15, 496).

|                                    |       |
|------------------------------------|-------|
| Water in 100 parts .....           | 39.73 |
| Solids        " .....              | 60.27 |
| Casein       " .....               | 24.84 |
| Fats         " .....               | 7.33  |
| Ash          " .....               | 4.02  |
| Milk-sugar, &c., in 100 parts .... | 3.54  |

The quantity of water varies 2 or 3 per cent. in different samples. W. N.

**Examination of Danish Export Cheese.** By V. SPORCH (*Bied. Centr.*, 1880, 366—370).—This paper is an exhaustive report of numerous experiments on the composition of Danish cheese, and is accompanied by various tables. The first question examined was the effect of leaving the milk a longer or shorter time before skimming or curding, and he found that practically the amount of cheese obtained varied very little, except in those intended to contain the fat of the milk. In such cases prompt treatment is the most desirable, but in cheese which is made from skimmed milk the difference arising from delay is extremely small. The water in skim-milk cheese varies considerably, from 58.65 to 69.31 per cent. The author believes that it exists in combination with the casein as a hydrate.

The temperature at which the operations should be conducted is an important point. At a low temperature a fatter cheese is obtained than at a higher, and a low temperature yields a cheese with

a larger proportion of water. The cutting and stirring of the curd should also be performed as soon as possible after the addition of the rennet, and when the milk begins to curd. The loss of weight which cheese experiences when stored is loss of water. The decomposition into ammonium compounds takes place only on the surface. The insoluble combinations are removed by the brushing, scraping, &c., to which the goods are often subjected.

Microscopically examined, cheese consists of a mass of casein confining innumerable fat globules, giving to it the appearance of a fine network, fat or creamy cheeses owing their softness in the mouth to the thinness of the cells which confine the globules. A good method of observing this structure is to stain a piece with methylaniline, the casein taking the colour, whilst the fat globules do not. J. F.

**Cleansing Lupines.** By O. KELLNER (*Bied. Centr.*, 1880, 515—517).—After steeping for 36 hours in cold water, the seeds are subjected to the action of steam for one hour, and then transferred to vats and washed with cold water, the latter being changed four times in 40 hours. By this means the alkaloïds are removed with very little loss of protein, the greatest loss occurring in the non-albuminous parts of the seed. J. K. O.

**Weighting of Silk.** By E. KÖNIGS (*Dingl. polyt. J.*, 237, 73—76).—The author examined a sample of black French silk from a consignment which spontaneously ignited on board a Bremen steamer. Treating with cold soda-lye and hot oxalic acid does not give concordant results as to the amount of weighting; also, the amount of ash bears no definite relation to the adulteration. Undyed raw silk gave 1.1 per cent. ash, scoured silk 0.77, and weighted silk 1.4. The relation borne by ash to the various substances employed was determined, and by calculation the amount of admixture was ascertained. Analyses (a) of the warp, and (b) of the weft, gave as follows:—

|                             | (a)   | (b)   |
|-----------------------------|-------|-------|
| Moisture.....               | 10.84 | 10.89 |
| Prussian blue.....          | 7.40  | 8.15  |
| Gum .....                   | 3.00  | —     |
| Fat .....                   | trace | 2.48  |
| Catechu-tannate of tin..... | 3.33  | —     |
| Tin ferrocyanide .....      | —     | 0.70  |
| Ash .....                   | 10.04 | 12.74 |

After taking from the ash, a, the tin oxide found, 1.8 per cent., iron oxide 4.9, corresponding to the Prussian blue, and 0.4 of ash due to the silk itself, there remains 2.94 per cent. iron oxide, corresponding to 21.17 per cent. catechu-tannate of iron, and only 54.26 per cent. of raw silk. This corresponds to 60.14 per cent. of scoured silk, after adding 5.88 of moisture; and 100 lbs. of raw silk give 152.32 of warp. Similarly b gives 9.35 per cent. of iron oxide in excess, corresponding to 47.68 per cent. of iron tannate, which gives 35.10 per cent. of raw silk. Adding 3.82 of moisture, this equals 38.92 of normal silk, which

with 64.9 — 3.82 equals 61.08, or 157 per cent. of loading. The weighting of the web is usually attained by the use of iron pyrolignite and catechu or chestnut extract, then potassium ferrocyanide and a little tin salt, and finally a tolerable amount of fat. Experiments showed that tannin compounds with some iron salts give bodies which easily take fire like tinder. On the contrary, tannin compounds produced with iron acetate are difficult to ignite, so that if the iron pyrolignite could be replaced by acetate the danger of spontaneous combustion would be removed.

J. T.

**"Mogdad" Coffee.** By J. MOELLER (*Dingl. polyt. J.*, 237, 61—63).—The author describes microscopically a sample of so-called "Mogdad" coffee, seeds of *Cassia occidentalis*, L. It can be detected by means of the microscope when added to coffee. J. J. Pohl gives the following analysis of the seeds:—

|   |       |
|---|-------|
| Cellulose .....                           | 21.21 |
| Fatty oil .....                           | 2.55  |
| Mucilage .....                            | 36.60 |
| Tannic acid (green with Fe).....          | 5.23  |
| Inorganic salts.....                      | 4.33  |
| Nitrogenous organic matter (and loss).... | 15.13 |
| Non-nitrogenous organic matter .....      | 3.86  |
| Caffeine.....                             | 0.00  |
| Water .....                               | 11.09 |

100.00

J. T.

**Wild and Cultivated Raspberries.** By E. REICHARDT (*Arch. Pharm.* [3], 15, 324—325).—A comparison of the fruit in a fresh condition showed that from the cultivated berries 90.4 per cent. of juice could be expressed, and only 81.64 from the wild ones. Amongst other results given in the paper, it is stated that the amount of acid was about equal in both, that the cultivated contained 4.45 per cent. of sugar and the wild only 2.80, and whilst the wild contained 2.80 per cent. of carbohydrates convertible by acids into sugar, the percentage in the cultivated was only 0.45. Cellulose was present in the wild berries to the extent of 4.15, and in the cultivated it amounted only to 2.26.

The comparison in the above particulars is evidently favourable to the cultivated fruit, and in respect of aromatic principles the advantage seems to lie in the same direction.

F. C.

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ERRATA.

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| 69   | 22        | <i>for</i> criticised <i>read</i> confirmed.  |
| —    | 25        | „ but „ and that.   |
| 110  | 13 and 14 | from bottom, <i>for</i> dimethyl- <i>p</i> -phenylenediamine ethoxamate <i>read</i> ethylic dimethyl- <i>p</i> -phenylenediamine-oxamate. |
| 182  |           | In the table at bottom of the page, cols. 3 and 4 give sp. heat of equal weights of the soil, cols. 5 and 6 that of equal vols.           |
| 248  | 13        | from bottom, <i>dele</i> "Acid."  |
| 249  | 16        | from top, <i>for</i> dimethyl methylpyrogallate <i>read</i> dimethylic methylpyrogallate.   |
| 330  | 8         | In this abstract <i>for</i> "fibrin" <i>read</i> "fibre" or "cellulose."  |
| 465  | 5         | <i>for</i> hypochlorous* <i>read</i> hydrochloric.  |
| —    | 18        | „ iodide „ chloride.  |
| 855  | 2         | from top, <i>for</i> $\frac{-O}{2}$ <i>read</i> $-\frac{O}{2}$ .  |
| 858  | 1         | „ <i>dele</i> "and."  |
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| 860  | 21        | „ „ 9.18 <i>read</i> 0.18.  |
| —    | 22        | „ „ 2.99 „ 2.92.  |

\* This error occurs in the original paper.





**I. A. R. I. 75.**

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